

Alma Mater Studiorum Università di Bologna Archivio istituzionale della ricerca

Geothermometric Constraints on the Thermal Architecture, Metamorphism, and Exhumation of the Northern Range, Trinidad

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

Gennaro, I., Weber, J., Vitale Brovarone, A., Arkle, J., Chu, X.u. (2022). Geothermometric Constraints on the Thermal Architecture, Metamorphism, and Exhumation of the Northern Range, Trinidad. JOURNAL OF METAMORPHIC GEOLOGY, 41, 1-23 [10.1111/jmg.12697].

Availability:

This version is available at: https://hdl.handle.net/11585/905011 since: 2023-03-01

Published:

DOI: http://doi.org/10.1111/jmg.12697

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (https://cris.unibo.it/). When citing, please refer to the published version.

(Article begins on next page)

This is the final peer-reviewed accepted manuscript of:

Gennaro, Ivano; Weber, John; Vitale Brovarone, Alberto; Arkle, Jeanette; Chu, Xu: Geothermometric Constraints on the Thermal Architecture, Metamorphism, and Exhumation of the Northern Range, Trinidad

JOURNAL OF METAMORPHIC GEOLOGY vol. 41 ISSN 0263-4929

DOI: 10.1111/jmg.12697

The final published version is available online at: <u>https://dx.doi.org/10.1111/jmg.12697</u>

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<u>https://cris.unibo.it/</u>)

When citing, please refer to the published version.

1 Geothermometric Constraints on the Thermal Architecture, Metamorphism, and Exhumation of

2

the Northern Range, Trinidad

Ivano Gennaro^{1*+}, John Weber², Alberto Vitale Brovarone^{3, 4, 5}, Jeanette Arkle⁶, Xu Chu¹ 3 ¹Department of Earth Sciences, University of Toronto. Toronto, Ontario M5S 3B1, Canada 4 5 ² Department of Geology, Grand Valley State University. Allendale, Michigan 49401, USA 6 ³ Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Alma Mater Studiorum Università di Bologna, Bologna, 7 Italy. 8 ⁴ Sorbonne Université, Museum National d'Histoire Naturelle, UMR CNRS 7590, IRD, Institut de Minéralogie, des Physique de Matériaux et de Cosmochimie, Paris, France 9 ⁵ Institute of Geosciences and Earth Resources, National Research Council of Italy, Pisa, Italy 10 11 ⁶ Department of Geology, Augustana College, Rock Island, IL 61201, USA 12 13 14 15 16 17 *Ivano Gennaro: ivanogennaro@gmail.com; https://orcid.org/0000-0002-9903-781X 18 John Weber: weberj@gvsu.edu 19 Alberto Vitale Brovarone: alberto.vitaleb@unibo.it 20 Jeanette Arkle: jennyarkle@augustana.edu; https://orcid.org/0000-0003-0640-6178 21 Xu Chu: xu.chu@utoronto.ca; https://orcid.org/0000-0002-6816-1076 22 23 † Current institute: Département de Sciences de la Terre, Université de Genève, 1205 Genève, Switzerland 24 25 26

Z/ Kummig Hue	27	Runnin	g Title
---------------	----	--------	---------

28 Thermal architecture of the Northern Range

29

30 Keywords

31 RSCM geothermometry, Trinidad, Geothermometry, Caribbean tectonics

32

33 Data Availability

- The data presented here as supplemental material (Tables S1 and S2) are openly available on the
- 35 PANGAEA Database and may be accessed under the DOI:
- 36 https://doi.pangaea.de/10.1594/PANGAEA.932772

37

38 Abstract

The Northern Range of Trinidad is composed of Mesozoic passive margin sedimentary rocks 39 40 that underwent ductile deformation and sub-greenschist to greenschist facies metamorphism in the early 41 Miocene. Previous studies identified a westward increase in the metamorphic grade but were unable to resolve whether this trend was discrete or continuous. In this study, we use Raman spectroscopy on 42 43 carbonaceous materials (RSCM) to constrain peak temperatures across the Northern Range with a greater resolution than was available in previous studies. These data are then combined with published 44 thermochronological data to constrain the tectonic history of a range-cutting fault that had been 45 previously inferred in previous geologic mapping. The RSCM temperatures show an abrupt increase 46 from 337 ± 10 °C in the east to 442 ± 16 °C west of the Chupara Fault at Chupara Point. Our RSCM-47 derived peak metamorphic temperatures are 50–100 °C higher than those from previous estimates, 48 requiring revision of tectonic models to account for deeper burial and greater exhumation. The peak 49 metamorphic conditions determined here, and our inferred timing of faulting, are consistent with the 50 51 two-stage tectonic model proposed in previous studies. A two-sided wedge formed during oblique plate collision and mountain building (stage I). Cooling rates differed in the Northern Range between eastern 52 and western blocks between $\sim 10-4.5$ Ma; this difference is attributed here to the activity along the cross-53 54 range Chupara Fault. This pattern of differential cooling, bedrock exhumation, and inferred bedrock and surface uplift may be associated with plate-scale strike-slip tectonics and the passage of a crustal-scale 55 bulge induced by deep tearing of South American lithosphere (stage II). 56

57

58 1. INTRODUCTION

Trinidad, the largest island in the nation of Trinidad and Tobago, is the southeastern-most island 59 60 in the Caribbean and is located in the Caribbean-South American plate boundary zone (Fig. 1a), where the Caribbean plate currently moves east relative to the South American Plate at a rate of ~20 mm/yr 61 (Weber, Dixon, et al., 2001). Current dextral plate motion is accommodated primarily along the Central 62 63 Range Fault, which strikes NEE-SWW through the middle of the island (Weber, 2009; Weber, Dixon, et al., 2001). The Northern Range, composed of Mesozoic passive margin sedimentary rocks that were 64 metamorphosed in the early Neogene, exposes pre-transform tectonic structures. Plate convergence in 65 the early Miocene gave rise to shortening in the foreland fold-and-thrust belt and metamorphism at sub-66 67 greenschist to greenschist facies conditions in the Northern Range segment of the hinterland belt (Algar & Pindell, 1993; Frey et al., 1988; Weber, Ferrill, et al., 2001). Following the culmination of contraction 68 and burial, exhumation of the hinterland metamorphic rocks took place from the Miocene to Pliocene, 69 70 which is thought to have resulted from an oblique Caribbean-South American Plate collision (Algar & 71 Pindell, 1993; Weber, Ferrill et al., 2001) and/or propagation of a deep-seated lithospheric tear fault (Arkle et al., 2017, 2021; Clark et al., 2008). The post-peak-metamorphic structures of the Northern 72 Range preserve the history of the regional exhumation kinematics (Weber, Ferrill et al., 2001), but the 73 74 general low grade of the Northern Range rocks limits the utility of conventional geothermometers for accurately assessing metamorphic conditions and changes. Illite crystallinity measurements, carbonate 75 76 thermometry, muscovite-paragonite geothermometry, and mineral equilibria were used to establish 77 baseline metamorphic conditions (Frey et al., 1988; Weber, Ferrill, et al., 2001). Using temperature-78 sensitive quartz and calcite microstructures, Weber, Ferrill, et al. (2001) were the first to recognize a systematic increase in deformation temperatures from east to west. However, this method involved high 79

uncertainties in temperature estimates, making it difficult to identify whether this temperature gradient is
continuous or segmented by discrete structures.

82 Raman spectroscopy on carbonaceous material (RSCM) is applicable to a wide range of 83 lithologies within metamorphic terranes; it is particularly powerful in resolving low-grade peak metamorphic temperatures, such as those in the Northern Range. This geothermometric technique 84 85 utilizes the crystallinity of carbonaceous material (CM) within the temperature range of 150-650 °C (Aoya et al., 2010; Beyssac et al., 2002; Kouketsu et al., 2014; Lahfid et al., 2010). With increasing 86 metamorphic temperatures, amorphous CM evolves towards turbostratic carbon and then graphitic 87 88 carbon through the process of graphitization, which is reflected in the relative areas of graphite and 89 defect bands in Raman spectra (Beyssac & Lazzeri, 2012; Beyssac et al., 2002; Lahfid et al., 2010; Wopenka & Pasteris, 1993). Because graphitization is theorized to be an irreversible process, the 90 crystallinity and Raman spectra of the CM should record peak metamorphic temperature conditions 91 92 (Beyssac & Lazzeri, 2012; Beyssac et al., 2003). It is important to ensure quality sample collection and 93 preparation for RSCM analysis, as for example, brittle deformation can affect the CM structure and therefore the calculated metamorphic temperatures (Nakamura et al., 2015; Kirlova et al., 2018). When 94 95 high-resolution RSCM is combined with a high sample density this geothermometer can identify 96 structural features not seen using less accurate methods (e.g., see Fig. 3 of Vitale Brovarone & Agard, 2013). The technique has been applied in a variety of metamorphic environments, from high-pressure 97 98 terranes to contact aureoles (Bayet et al., 2018; Beyssac et al., 2019; Lahfid et al., 2010; Molli et al., 99 2018; Rahl et al., 2005; Simoes et al., 2007; Vitale Brovarone & Agard, 2013; Vitale Brovarone et al., 2013). 100

The Northern Range rocks and structures are deeply weathered, covered by dense tropical
 vegetation, and, aside from excellent coastal and stream exposures, are generally poorly exposed and

difficult to access. Thus, previous structural studies have produced contradicting maps and 103 104 interpretations (see below). In this study, we approach some of the unsolved structural and kinematic 105 problems from a metamorphic perspective. Specifically, we use RSCM geothermometry to determine the peak metamorphic temperatures for a robust suite of Northern Range samples from east to west 106 107 across the range (Fig. 2). We aimed to resolve the field gradient and to provide new temperature 108 constraints to better establish the thermal architecture of the Northern Range. These new constraints help 109 us determine whether the Northern Range was exhumed as a single rigid block or as discrete, fault-110 bounded range segments. Our new RSCM data, combined with previously published geological maps and thermochronological data, confirm the presence of a large-scale, cross-range, crustal-scale fault, the 111 Chupara Fault, which was previously mapped but only poorly defined. Based on our new RSCM 112 constraints, we review and modify existing tectonic models to explain the metamorphic, emplacement, 113 and exhumation history of the Northern Range. The results presented here explore the thermal 114 115 architecture and tectonic evolution of a mountain range formed in plate boundary that transitioned from 116 collisional to transform, providing a real-world laboratory to examine processes that can then be used to better constrain geodynamic models (e.g. Govers & Wortel, 2005). 117

118

119 2. TECTONIC FRAMEWORK AND GEOLOGIC HISTORY

The Caribbean plate is postulated to have developed from the Caribbean large igneous province, an oceanic plateau or hotspot swell that formed from 139–83 Ma far west of its current location (Burke, 1988; Hoernle et al., 2004). The Caribbean plate began migrating eastward and entered the gap between the North and South American plates near the end of the Cretaceous (~66 Ma), and it eventually collided with northwestern South America (Kennan & Pindell, 2009) and southern North America. The rocks of the Northern Range were presumably derived from passive margin sediments deposited along the northern edge of South America (Frey et al., 1988; Robertson & Burke, 1989). These sedimentary rocks
underwent low-grade metamorphism, with sub-greenschist mineral assemblages present in the east and
greenschist assemblages present in the central and western Northern Range (Frey et al., 1988, Weber,
Ferrill, et al., 2001). The presence of slates, marbles, quartzite and schists, as well as their detrital zircon
U-Pb age spectra, supports a passive margin provenance for these rocks (Bartlett et al., 2021).

131 Zircon fission-track thermochronology data was used to suggest that the initial phase of 132 metamorphism and deformation in the Northern Range may have started as early as the late Eocene (Algar & Pindell, 1993), but this interpretation was based on partially reset samples and from only a 133 134 limited portion of the range. Subsequent studies used apatite fission track and apatite and zircon (U-Th)/He data to revealed that the initial exhumation of the Northern Range occurred ~10-8 Ma in west 135 and ~6–4 Ma in the east (Arkle et al., 2021). Hinterland structural and metamorphic events are most 136 clearly delineated in the western Northern Range. White mica ⁴⁰Ar/³⁹Ar ages date peak metamorphism 137 in the Northern Range between 23 Ma and 34 Ma (Foland et al., 1992; Speed et al., 1997; Weber & 138 139 Arkle, 2015). Syn-metamorphic deformation (isoclinal F_1 folding, transposition of original bedding, and S_1 foliation development) was followed by a second F_2 folding event and the development of S_2 140 crenulation cleavage (Weber, Ferrill, et al., 2001). The general picture is that plate-scale transpression 141 142 drove high magnitude crustal shortening and exhumation in the southern Caribbean metamorphic hinterland, which includes the Northern Range (Cruz et al., 2007; Weber, Ferrill, et al., 2001). The main 143 144 stages of deformation and exhumation in the hinterland belt are largely coeval with folding and thrusting in the Trinidad foreland, i.e., the Central and Southern Ranges. Deformation and exhumation in the 145 146 Central Range is constrained to have occurred in the mid-Miocene (11–18 Ma) by using stratigraphy and zircon (U-Th)/He dating (Giorgis et al., 2017). 147

148 A late stage of deformation (D_3) within the Northern Range is recorded as a series of steeply

dipping normal faults that strike SE-NW and NE-SW and crosscut previous fabric elements (Fig. 2;
Kugler, 1961; Weber, Ferrill, et al., 2001). These faults have been interpreted as related to E-W
transform shear, and as such, these faults may accommodate transtension associated with relative
Caribbean-South American strike-slip motion (Algar & Pindel, 1993). Thus, Flinch et al. (1999) posit
that these D₃ faults formed during or after the late Miocene or Pliocene.

154 Many different scenarios have been proposed to explain the metamorphism and exhumation of 155 the metamorphic hinterland belt along northern South America. A few works advocate for the oblique 156 collision and subduction of South America beneath the Caribbean plate (Audemard, 2009; Cruz et al., 157 2007; Pindell & Kennan, 2001, 2007, 2009). Some oblique collision models require about 240 km of displacement since 12 Ma to bring the Northern Range into its current position (Pindell & Kennan, 158 159 2001). Exhumation of the Northern Range has been explained by isostatic rebound after forming a deep 160 crustal root that developed during an oblique collision (Algar & Pindell, 1993; Algar et al., 1998; Cruz 161 et al., 2007), or through the activation of late-stage, range-bounding brittle structures. Weber, Ferrill, et 162 al. (2001), for instance, initially called on differential dip-slip along the Arima Fault, a late south-sidedown normal fault bounding the southern Northern Range (Fig. 1b & 2), to explain differences in 163 eastern and western metamorphic grades. 164

Alternatively, metamorphism, deformation, and exhumation of the Northern Range could be associated with the passage of a lithospheric tear fault under Trinidad (Arkle et al., 2017, 2021; Clark et al., 2008; Levander et al., 2014). Currently, the subduction of the Atlantic oceanic lithosphere (of both the North and South American plates) under the Caribbean plate is accommodated by tearing of the lithosphere along a subduction-transform edge propagator (STEP, Fig. 1c; Govers and Wortel, 2005). STEP faults mark the transition between subduction and transform plate boundaries and are characterized by non-uniform relative plate motion; deformation, rotation, and uplift are often induced

along the transform side of the transition as the subducting plate is torn at the STEP edge (Govers & 172 Wortel, 2005). The active southeastern Caribbean STEP fault is marked by the Paria cluster of depth 173 earthquakes beneath the northern coast of eastern Venezuela (Fig. 1a), and the active STEP edge is 174 currently proposed to be positioned offshore eastern Trinidad, about 175 km east of the Paria cluster (c.f. 175 Fig. 2 of Nijholt & Govers, 2015). Some recent interpretations have postulated that exhumation of the 176 177 Northern Range was driven by STEP fault processes including the detachment of the South American lithosphere, asthenosphere flow, and flexural bulging ahead of the STEP tear (Arkle et al., 2017; 2021; 178 179 Clark et al., 2008; Levander et al., 2014). Accordingly, eastward propagation of the Caribbean plate and 180 associated STEP fault caused the observed asymmetric exhumation, and the thermochronological ages from the region that increase eastward and post-date the presumed oblique collision (Arkle et al., 2021). 181 STEP-induced deformation also fits the observed Quaternary tectonic inversion and asymmetry of slow 182 eastern and fast western exhumation rates (Arkle et al., 2017; Clark et al., 2008; Levander et al., 2014). 183 Differences between regional tectonic models germane to this study are whether the hinterland 184 185 metamorphic rocks are allochthonous and disconnected with folding and thrusting in the foreland or parautochthons and connected with foreland deformation in space and time. 186

187

188 **3. GEOLOGIC SETTING AND SAMPLE DESCRIPTION**

189 **3.1 Structures and Stratigraphy**

The Northern Range of Trinidad is bounded by the Arima Fault to the south and the Northern
Coast and Sub-Tobago Terrane faults offshore to the north (Fig. 1b) (Robertson and Burke, 1989; Weber
et al. 2015, 2020). The Arima Fault was originally mapped by Kugler (1961) and corresponds to
observable meso-scale faults and cataclastic zones (Weber, Ferrill et al., 2001). Previously hypothesized

to be an eastward extension of the El Pilar transform fault, the Arima Fault is actually a south-side-194 down, inactive normal fault that accommodated N-S extension (Weber, Ferrill et al., 2001). The 195 196 subsurface Caroni fault may instead represent the eastern El Pilar extension (Pindell & Kennan, 2007), though active strike-slip motion now occurs along the Central Range Fault to the south (Fig. 1b; Weber, 197 Dixon, et al., 2001). The North Coast and Sub-Tobago Terrane fault zones (Fig. 1b) accommodate active 198 199 strike-slip and normal dip-slip between the Northern Range and Tobago terrane (Robertson & Burke, 200 1989; Weber et al. 2015, 2020). This offshore fault zone also contains *en echelon* normal faults that 201 strike northwest and have moderate to steep northeastern dips (Robertson & Burke, 1989). These en 202 echelon structures mirror the late normal faults mapped and observed in the Northern Range at the meso- and macro-scales (Fig. 2) and are attributed by Robertson & Burke (1989) to be related to broad, 203 plate-scale, transform shear. Such structures are also mapped in eastern Paria (Cruz et al., 2007). 204

At Chupara Point, both Kugler (1961) and De Verteuil et al. (2005) infer the presence of the 205 206 Chupara Fault, a northwest-striking, steeply dipping, west-side-up normal fault. The inferred Chupara 207 Fault trends NNW-SSE from Chupara Point on the north coast, across the range, potentially extending across the entire range southward to where it is truncated by the Arima Fault near the town of Maturita 208 (Fig. 2; Kugler, 1961; De Verteuil et al., 2005). On the other hand, Potter (1968) inferred a series of 209 210 short, disconnected, NW-striking fault segments at Chupara Point, Verdant Vale, and along the southern foot of the range. Kugler (1961) mapped the Chupara Fault as one in a series of southeast- and 211 212 southwest-striking normal faults. Some of the other geologic maps of the range do not show the Chupara 213 Fault (e.g., Saunders et al., 1997). Mapping the Northern Range has been a significant challenge. 214 Kugler's (1961) biostratigraphic approach that proved so successful in Trinidad's sedimentary rocks further south, together with related attempts to establish a protolith stratigraphy in these metamorphic 215 rocks, has largely failed (see below). 216

217	The metasedimentary rocks of the Northern Range include predominantly slates, quartz and mica
218	schists, quartzites, and metacarbonates. Mesozoic fossils have been reported from only about a dozen
219	localities scattered in the range (e.g., Dighton-Thomas, 1935; Imlay, 1954; Kugler, 1961; Saunders,
220	1972; Spath, 1939; Trechmann, 1935); these ages range from Tithonian (Jurassic) (?) to Maastrichtian
221	(Upper Cretaceous) (Fig. 2). Significantly, relict fossils have only been found in the low-grade rocks
222	east of the inferred Chupara Fault and in the fault-bounded, low-grade Laventille metalimestone and
223	Lopinot phyllite along the range front. Apparently, no relict fossils have survived in the higher-grade
224	metamorphism west of the Chupara Fault, which have been isoclinally folded, structurally transposed
225	(i.e., original bedding has been rotated into, cut by, and highly stretched in the S1 foliation), and highly
226	recrystallized. In addition to the relict fossils, two radiometric ages that are highly disparate have been
227	reported from the San Souci metabasalt, which is a small and significant, but poorly studied, poorly
228	mapped, and poorly understood meta-igneous unit in the range (Fig. 2). Wadge & Macdonald (1985)
229	report a whole rock K-Ar protolith age of 87 ± 4.4 Ma, whereas Neill et al. (2014) dismiss the earlier
230	age as erroneous due to alteration and report a 135 ± 7.3 Ma zircon U-Pb crystallization age.
231	Traditionally it has been assumed, though not demonstrated, that a simple protolith stratigraphy
232	still exists in these metamorphic formations, despite the limitations discussed above, and the fact that
233	they are indeed metamorphic rocks, not sedimentary rocks (Algar & Pindell, 1993; Barr, 1965; Kugler,

1961; Potter, 1973; Saunders, 1997). Even in the western Northern Range, where relict fossils are
completely absent, this imagined protolith stratigraphy leads to the erroneous, widespread, and still
recently circulating interpretation that the megastructure of the Northern Range is a northward-vergent,
overturned, macroscopic anticline (Kugler, 1961; Potter, 1973; Algar and Pindell, 1993; Babb & Mann,
1999). Instead, the sheet dip of the bedding-parallel S₁ foliation is consistently toward the south there
and forms a homocline in which the resistant metamorphic units (quartz schists and quartzites) form a

series of south-dipping dip-slopes and hogbacks. The De Verteuil et al. (2005) map is the first attempt to
abandon the hypothesized protolith stratigraphy and simply map metamorphic rock types as directly
observed in the field. We follow a similar approach below as we describe and treat the units in the
Northern Range as low-grade metamorphic terranes.

244 **3.2 Petrography and Sample Descriptions**

245 Northern Range protoliths were likely derived from passive margin sediments deposited along the northern edge of South America during and after the breakup of Pangea in the Jurassic and 246 247 throughout the Cretaceous (Speed, 1985; Frey et al., 1988; Robertson & Burke, 1989; Bartlett et al., 2021). These protoliths were likely carbonates, mudstones, and sandstones, which have been 248 249 metamorphosed at sub-greenschist to greenschist facies conditions (Frey et al., 1988). The protoliths 250 represent a mixture of continental shelf sedimentary rocks that were deformed and exhumed during and after Miocene collision (Pindell & Kennan, 2001, 2007). The twenty-six samples we collected and 251 252 analyzed are representative of the six major lithologies from across the Northern Range (Fig. 2) (1) 253 high-grade, foliated marble, (2) low-grade metacarbonate, (3) mica schist, (4) mica-rich phyllite, (5) metasandstone, and (6) carbon-rich slate (Fig. 2 & 3). 254

The high-grade marbles (Fig. 3a) are all strongly foliated, exhibiting dark bands rich in CM and 255 lighter, carbonate-rich bands. Many of these samples also contain minor sulfides, mainly pyrite and 256 arsenopyrite; some of the pyrite grains have been weathered and broken down into iron oxides. The low-257 258 grade metacarbonates (Fig. 3b; metacarbonate in Fig. 2) generally preserve primary sedimentary 259 structures and textures (Fig. 3c). Fossil shells and ooids are common in many of these rocks, which 260 exhibit low-strain, ductile deformation at the micro-scale (Fig. 3c). Some low-grade metacarbonates are 261 crosscut by calcite-filled veins indicative of brittle extensional deformation and precipitation from metamorphic fluids. Further, later stage brittle deformation is recorded by the cross-cutting of calcite 262

veins by fractures.

The quartz-mica schists (Fig. 3d) mainly crop out in the western Northern Range. These schists 264 are well-foliated and consist of a greenschist-facies mineral assemblage (muscovite + chlorite + quartz + 265 plagioclase + CM \pm biotite \pm oxides or sulfides). These rocks are variable in both composition and 266 structure, showing a wide range of mica content (5-25%). Coarser-grained rocks tend to have less mica 267 268 and a less evident foliation. These are the only rocks seen to host metamorphic biotite in substantial quantities, indicating they are likely of the highest grade in the study area. Quartz and calcite grains in 269 270 these rocks are thermally recrystallized, as indicated by the presence of undulose extinction in quartz 271 and the presence of triple-point grain boundaries (Fig. 3d). Recrystallization likely occurred during deformation, as evidenced by the oriented stretching elongation of quartz parallel to the S_1 foliation 272 plane (Fig. 3d). This elongation is consistent with the observations of Weber, Ferrill, et al. (2001), who 273 attributed the foliation to the first stage, D_1 , of Northern Range deformation. At the microscopic scale, 274 275 CM is observed to be concentrated in mica-rich bands related to the tight F_1 folds that transpose bedding 276 (S_0) into S_1 and later kink bands.

The phyllites (Fig. 3e) are extremely rich in sericite, and are fine-grained, and well foliated. The 277 phyllitic foliation is defined by sericite \pm chlorite, with some degree of post-S₁ crenulation common in 278 279 these rocks. The multiple foliation planes recorded in these phyllites reflect the first two phases of Northern Range deformation, which predominantly occurred in the ductile regime (Weber, Ferrill, et al., 280 281 2001). The CM content of the phyllites is variable; only a few samples had sufficient CM for RSCM 282 analysis. Carbonaceous material with radial growth textures 0.1–0.3 mm in length is also observed in 283 some of these rocks and it appears to be post-kinematic as it crosscuts foliation (Fig. 3f); multiple explanations are possible for their formation (cf. Luque et al., 1998; Rumble, 2014). Their composition 284 was confirmed to be carbonaceous through electron probe microanalysis (EPMA). 285

Metasandstones are composed mainly of subangular quartz grains (Fig. 3g), but also contain 286 minor mica and calcite along with CM. The weakly-metamorphosed rocks of this type come from the 287 288 eastern and central Northern Range and are typically non-foliated to weakly foliated. Atypically strong foliation and folding were observed in sample NR-1 (Fig. 3h). Sample NR-1 (equivalent to NR-3) 289 displays isoclinal microfolds, likely representing parasitic folds created during early semi-ductile 290 291 deformation. Metasandstones from the central Northern Range display a weak foliation, but some quartz grains experienced modest shape changes, likely through a combination of pressure solution and low-292 293 temperature crystal plasticity (Weber, Ferrill, et al., 2001). Minor chlorite is seen in central Northern 294 Range samples. However, it is generally absent in the eastern metasandstones, reflecting either a variation in composition or metamorphic grade; limited evidence suggests the former (Frey et al., 1988). 295

The dark, carbon-rich slates (Fig. 3i) are compositionally and texturally similar to the phyllites, but tend to have a lower mica content and higher content of carbonate minerals (Fig. 4a) and CM. These rocks are very fine-grained and well foliated, containing minor amounts of quartz, plagioclase, and sulfides that mainly occur as framboidal pyrite. These rocks have a well-developed, early S₁ slaty cleavage that is weakly crenulated by subsequent deformation.

301 **4. METHODS**

302 4.1 Electron Probe Microanalysis

Quantitative wavelength-dispersive spectrometry and backscattered electron (BSE) imaging were
 carried out using a JEOL JXA-8230 electron probe microanalyzer (EPMA) at the University of Toronto.
 Quantitative analyses employed a 10 nA beam current, 15 kV accelerating voltage, and off-peak
 background corrections. The electron beam was defocused (10 µm) to minimize beam damage on
 carbonate minerals.

308 4.2 RSCM Geothermometry

309	Thin sections were polished to a thickness of \sim 35 μ m and made in accordance with the
310	specifications of Beyssac et al. (2003) for RSCM analysis. Rocks were cut perpendicular to bedding or
311	foliation planes and parallel to lineation in order to reduce within-sample heterogeneity caused by the
312	anisotropy of CM (Beyssac et al., 2003). The carbonaceous inclusions in transparent minerals were
313	analyzed using two Raman spectrometers: 15 samples were analyzed at the Department of Earth
314	Sciences at the University of Turin (UNITO) in Turin, Italy, and another 18 samples were analyzed at
315	the Royal Ontario Museum (ROM) in Toronto, Canada. Seven samples were analyzed on both
316	spectrometers to ensure inter-instrument consistency. Only one sample (DT-93-1) was omitted due to a
317	lack of CM.
318	Raman spectra were collected using a LabRAM HRVIS from Horiba Jobin Yvon Instruments at
319	UNITO and a Horiba LabRAM ARAMIS micro-Raman spectrometer at the ROM. Both spectrometers
320	were calibrated with a silicon standard and used a 532 nm solid-state neodymium laser. The lasers were
321	dispersed using 1200 gr/mm gratings and focused on the samples using 100x objectives with a
322	numerical aperture of 0.9. In order to avoid laser-induced heating, a low laser power (<5 mW) was used
323	during analysis (Beyssac et al., 2003). At UNITO, no filter was required; at the ROM, the D1 or D0.6
324	filters (10% and 25% transparency respectively) were used to ensure a laser power below 5 mW.
325	A combination of transmitted and reflected light was used to target CM located below the
326	surface of the host minerals to avoid artificial defects induced by sample preparation (Beyssac &
327	Lazzeri, 2012; Beyssac et al., 2003). At least 15 spectra were collected for each sample. The spectral
328	baselines were corrected, and the spectra were fitted using the Peakfit software (AISN Software Inc.,

1995). Wherever possible, a linear baseline was used for the correction, but micaceous samples

sometimes required a best-fit baseline correction as the fluorescence of mica is detectible within the
 range of 700–2000 cm⁻¹ (Beyssac & Lazzeri, 2012).

332 For samples showing CM Raman spectra characteristic of high-temperature conditions (>330 °C; 333 e.g., SC-2b, Fig. 5a), we apply the 532 nm laser-based calibration of Aoya et al. (2010) (Eq. 1) along with the 514 nm laser-based calibration of Beyssac et al. (2002) (Eq. 2) as a reference. These spectra 334 335 were fitted with three bands and Voigt peaks, which converged to a unique solution (Beyssac & Lazzeri, 2012; Lahfid et al., 2010). For samples showing CM Raman spectra characteristic of low-temperature 336 conditions (<350 °C; e.g., T94-3, Fig. 5b), we apply the 514 nm laser-based calibration of Lahfid et al. 337 338 (2010) (Eq. 3) and the two 532 nm laser-based calibrations of Kouketsu et al. (2014) (Eq. 4 & 5). For the 339 Lahfid et al. (2010) calibration, these spectra are decomposed into five bands; the use of Lorentzian profiles was necessary to reduce the degree of freedom and allow a unique solution to be obtained 340 (Beyssac & Lazzeri, 2012; Lahfid et al., 2010). The samples were then refit following Kouketsu et al. 341 342 (2014) to use their calibrations (see below). The temperatures were then calculated using the area ratios 343 of the peaks based on the respective thermometer calibrations (see Aoya et al., 2010; Beyssac et al., 2002; Lahfid et al., 2010). 344

345 Most samples displayed solely high- or low-temperature spectra, whereas nine samples of intermediate temperature (300–360 °C) feature a mixture of 3- and 5-band spectra. In the case of the 346 nine samples with both types of spectra, the Aoya et al. (2010) calibration was applied to 3-band spectra 347 348 and the Lahfid et al. (2010) calibration was applied to 5-band spectra. We note that only four reported temperatures are the averages of both calibrations that statistically overlap. The second calibration 349 350 applied to the other five samples is rejected as outliers (Table 1). For example, among the fifteen 351 datapoints of 93-T-CB, three 5-band spectra yield much lower temperatures (284 ± 10 °C) than the twelve 3-band spectra which make up the majority (366 ± 5 °C; Table S1). On the other hand, one 352

datapoint of MAT-1(3) shows a 3-band spectrum that yields a temperature of 472 °C, >100 °C higher than the average of the 5-band spectra (340 ± 4 °C); this CM inclusion, consistent with the temperature calculated using the Beyssac et al. (2002) calibration, is interpreted as detrital CM (Table S1). In both cases, the outliers were omitted when reporting the final temperature.

A second fitting of the data was done on samples with peak temperatures below 400 °C in 357 358 accordance with the specifications of Kouketsu et al. (2014). These calibrations utilize 3-5 peaks which 359 allow for the calculation of peak temperature based on the full width at half maximum (FWHM) of the 360 D1 and D2 bands (Kouketsu et al., 2014). A second fitting ensured all spectra treated were fit with a 361 linear baseline in the range of 1000–1750 cm⁻¹ with pseudo-Voigt (Gaussian-Lorentzian sum) functions in accordance with Kouketsu et al. (2014). Some peaks were fixed based on the characteristics of the 362 Raman spectra, such as the intensity ratio of the main D and G bands, to allow for convergence to a 363 364 unique solution (Kouketsu et al., 2014).

Following these calibrations, R2 and RA1 represent the area ratios between the main D band and the entire spectrum in high- and low-temperature samples, respectively, with FWHM_{Dx} representing the full width at half maximum of the corresponding defect band (D1 or D2) (Beyssac et al., 2002; Kouketsu et al., 2014; Lahfid et al., 2010).

369
$$T(^{\circ}C) = 221.0(R2)^2 - 637.1(R2) + 672.3$$
 (1)

370
$$T(^{\circ}C) = -445(R2) + 641$$
 (2)

371
$$T(^{\circ}C) = (RA1 - 0.3758)/0.0008$$
 (3)

372
$$T(^{\circ}C) = -2.15(FWHM_{D1}) + 478$$
(4)

373
$$T(^{\circ}C) = -6.78(FWHM_{D2}) + 535$$
(5)

374

375 **5. RESULTS**

376 5.1 Carbonate Thermometry

377 Weber, Ferrill et al. (2001) presented comprehensive documentation and analyses of the calcite 378 microstructures in the Northern Range metasedimentary rocks (see their Figure 8). Depending on the 379 metamorphic grade, the calcite microstructures range from thin calcite twins in rocks with intact and 380 preserved sedimentary textures to plastically deformed, fully recrystallized, mechanical twins. Given 381 that these dynamically recrystallized calcite grains are commonly present in crosscutting veins, the highest temperatures derived from calcite microstructures in that study can thus be considered as a lower 382 383 bound for peak metamorphic temperatures. Here, we attempt Ca-Mg-Fe thermometry between calcite 384 and dolomite in a slate sample with disseminated calcite and dolomite (NR-5, equivalent to NR-2), and 385 show that this thermometer is not applicable due to a lack of chemical and textural equilibrium.

386 A BSE image representative of the mineral assemblage and texture of NR-5 is presented in Figure 4a. Ankerite grains (dol in Fig. 4) are larger and more euhedral than calcite. The schistosity bends 387 and forms pressure shadows around ankerite micro-porphyroblasts. The ankerite has a Mg# (=Mg / [Mg 388 + Fe]) ~0.4 and Ca content ~0.54 per 3 O. The calcite contains minor (~0.04 per 3 O) Fe, Mg and Mn 389 (Fig. 4b). The bending of schistosity around both calcite and ankerite grains suggests that both are likely 390 pre-kinematic, potentially pointing to the presence of both minerals during peak metamorphism. 391 However, the two minerals show contrasting crystal habits, with euhedral ankerite exhibiting stability 392 while anhedral calcite grains likely reequilibrated with the surrounding matrix during retrograde 393 394 metamorphism.

Along with the disequilibrium textures, the analyzed carbonates display a high degree of 395 scattering on the carbonate phase diagrams, yielding a large temperature range (Fig. 4b). While the 396 thermodynamic models (Anovitz & Essene, 1987) include uncertainties and equilibrium assumptions, 397 the variability of measured carbonate concentrations adds to the concern of applying this particular 398 mineral-pair thermometer. Calcite microstructural geothermometry from the adjacent area yields 200– 399 400 250 °C (Weber, Ferrill, et al., 2001), but inferred phase relations suggest disequilibrium between calcite and dolomite at 250 °C (Fig. 4b). In contrast to the >300 °C temperature recorded by RSCM (see 401 402 below), the calcite composition and microstructures must have been modified during retrograde 403 metamorphism. In sum, as in Frey et al. (1988), conventional geothermometers could not resolve the field gradient across the low-grade eastern Northern Range due to the violation of several of the required 404 fundamental assumptions. 405

406 **5.2 RSCM Data and Thermometry**

Representative low-temperature and high-temperature Raman spectra are presented in Figure 5 407 to illustrate the decomposition of Raman spectra for RSCM calculation. A complete set of fitted spectral 408 data are provided in the supplementary material (Tables S1 & S2; Gennaro et al., 2021), and a complete 409 set of results based on spectra fitting are presented in Table 1. In the first-order region (700-2000 cm⁻¹), 410 the low-temperature and high-temperature samples show characteristic RSCM features such as the 411 presence of five (G, D1, D2, D3, D4) and three (G, D1, D2) major Raman bands, respectively (Fig. 5; 412 413 Beyssac & Lazzeri, 2012; Beyssac et al., 2002; Lahfid et al., 2010). Samples of intermediate temperature (~340–380 °C) were also fitted with four bands in accordance with Kouketsu et al. (2014). 414 Along with the major D and G peaks, spectra from carbonate-rich samples show calcite peaks at ~1100 415 cm⁻¹, which were minimized as much as possible in measurements. Values of the R² fitting correlation 416

417 coefficient on samples with calcite peaks may be low as this peak is removed after fitting to allow for418 calculations using only peaks associated with CM.

419 The centers of fitted G bands show moderate variation (Table S1; Fig. S1) from fully ordered 420 graphite (1582 cm⁻¹; Wang et al., 1990), especially the low-temperature samples analyzed at UNITO (Fig. S1). The downshifted Raman spectra might reflect amorphization by laser heating (Kagi et al., 421 422 1994; Iwasaki et al., 2013; Nakamura et al., 2019), as Raman spectra of low-grade CM are ideally obtained with laser powers of <1 mW to avoid laser-induced artifacts (Nakamura et al., 2019). 423 424 Nonetheless, we note that the apparent temperatures calculated using 3- and 5-band calibrations (Aoya et al., 2010 and Lahfid et al., 2010, respectively) do not show any systematic correlation with the shifts 425 of G bands (Fig. S1). Given that the intrinsic uncertainty of RSCM on low-grade samples is unquantified 426 427 and potentially considerable, we reasonably regard the temperatures as robust results.

The temperatures from the two Kouketsu et al. (2014) calibrations display up to 100 $^{\circ}$ C 428 429 variations between the temperatures calculated using the two calibrations on the same sample (Fig. 6 inset). The FWHM of G and D bands has been known to vary as a result of laser-induced heating at laser 430 powers above 1 mW, thus laser-induced heating is the likely cause of this discrepancy (Iwasaki et al., 431 432 2013, Nakamura et al., 2019). This is especially evident if the downshift of the G band is used as a proxy for laser-induced heating. Samples with higher scatter in the position of the G band tend to show greater 433 434 disagreement between the D1- and D2-based calibrations of Kouketsu et al. (2014) (Fig. S1). Therefore, 435 while laser-induced heating does not significantly affect the temperatures of the Aoya et al. (2010) or Lahfid et al. (2010) calibrations in our analysis, the temperatures derived from the Kouketsu et al. 436 (2014) thermometer are considered to be significantly altered and are not used for interpretation. 437 Our new RSCM temperatures range from 310 ± 13 °C to 465 ± 30 °C (Lahfid et al. 2010 and 438

439 Aoya et al. 2010 calibrations; 1σ), with an outlier at 497 ± 27 °C (sample M-4). Figure 5c shows the

evolution of the acquired spectra with increasing metamorphic temperature. The spectral evolution shows an increase in the intensity ratio of the main D and G bands (I_D/I_G) until about 350 °C, where the main G peak then begins increasing in intensity and area as the D peak decreases. In low-temperature spectra, the D3 and D4 bands decrease in area as temperature increases, and they disappear at around 350 °C. Above this threshold, the D1 and D2 bands decrease in area relative to the G composite band, suggesting progressive graphitization (Beyssac et al., 2003).

We also assess the inter-instrument correlation between the spectra collected at UNITO and the 446 ROM, plotting the calculated temperatures from both spectrometers against a 1:1 line (Fig. 6). The 447 reproducibility of the high-temperature spectra is very good. However, the lower temperature spectra 448 display a larger inter-instrument error regardless of the calibration used. A degree of inter-instrument 449 450 error is to be expected, has been observed in the past, and is caused by differences in analytical settings such as laser power, the instrument's CCD, and slit spacing on the diffraction grating (Lünsdorf et al., 451 2013). The increased inter-instrument error in the low-temperature region may be due to differences in 452 453 laser power, despite being kept below 5 mW, as laser-induced heating may still induce defects in the Raman spectrum at this energy, especially in highly amorphous CM (Beyssac et al., 2003, Kagi et al., 454 1994; Iwasaki et al., 2013; Nakamura et al., 2019). With regards to the scatter of low-temperature data, 455 456 the calibrations for low-temperature spectra are more complex as graphitization below 330 °C is affected by variables other than just temperature (Lahfid et al., 2010). Furthermore, the RSCM calibrations, 457 especially at low temperatures, are highly sensitive to the fitting and baseline correction method used 458 459 (Beyssac & Lazzeri, 2012; Lünsdorf et al., 2013). For consistency, and to reduce the variability caused 460 by inter-instrument error and laser-induced heating, samples from the ROM were used in all cases where 461 samples were analyzed using both spectrometers.

The spatial variation of temperatures exhibits an increase from east to west across the Northern 462 Range (Fig. 7a), in agreement with previous studies (Frey et al., 1988; Weber, Ferrill, et al., 2001). The 463 464 Lahfid et al. (2010) RSCM results yield temperatures around 320 °C in the easternmost parts of the Northern Range, which increase westward to about 360 °C in the central Northern Range (Fig. 7b). 465 Temperatures of ~360 °C in the central Northern Range are predicted by both low-temperature 466 467 calibrations. An abrupt temperature difference is seen in the central Northern Range across the previously mapped Chupara Fault (De Verteuil et al. 2005; Kugler, 1961). To the west of this fault, 468 469 RSCM records peak temperatures of around 450 $^{\circ}$ C, except for the two samples at ~420 $^{\circ}$ C in the 470 vicinity of the fault. The temperature difference between the eastern (337 \pm 10 °C; Lahfid et al. (2010) calibration) and western segments (442 \pm 16 °C; Aoya et al. (2010) calibration), within ~5 km, is 105 \pm 471 19 °C, and a two-tailed Student's t-test indicates that the means are statistically different at the 99% 472 confidence level. Qualitative observation of the Raman spectra corroborates the significant temperature 473 474 difference between the eastern and western samples. The presence of significantly different Aoya 475 temperatures in the east and west further corroborates this difference as these were derived using the same calibration and represent a degree of internal consistency. The temperatures are internally 476 consistent within the western block, with the eastern block showing higher variation, particularly in the 477 478 easternmost regions of the Northern Range. Samples in the east gradually increase in temperature from east to west, though they remain close to 340 °C. In addition, samples in the southwestern Northern 479 480 Range are bounded by the Arima Fault and perhaps additional bounding faults, and typically show lower 481 temperatures (350–410 °C) than their northwestern counterparts (~450 °C; Fig. 7a).

482 **6. Discussion**

483 6.1 Metamorphic Field Gradient and Faulting

Our RSCM data not only corroborate the existence of a geothermal gradient across the Northern 484 Range, but now resolve that this gradient is discrete. The thermal discontinuity in the central Northern 485 Range (Fig. 7a, b) juxtaposes high- (442 \pm 16 °C) and low-temperature (337 \pm 10 °C) blocks at Chupara 486 Point. Given the abrupt temperature change we observe, a structural discontinuity must exist to 487 accommodate it. The most probable candidate for such an intra-range boundary is the Chupara Fault as 488 489 mapped by Kugler (1961) and De Verteuil et al. (2005). The Chupara Fault is one in a series of SEstriking normal faults that were hypothesized by Algar & Pindell (1993) to represent the final, 490 491 transtensional stage of Northern Range deformation and presumed to be related to a change in the 492 direction of Caribbean-South American plate motion from collisional to right-lateral strike-slip (transform). 493

Much of our RSCM data comes from the north coast, leaving the southern mountain front and 494 internal segment of the metamorphic discontinuity more poorly constrained. Here, we refine slightly the 495 Chupara Fault trace as mapped by De Verteuil et al. (2005), which was based on differences in 496 497 metamorphic rock types and inferred differences in grade using microstructures. Topographic radar images show possible minor differences across the northern trace of the Chupara Fault; these diminish to 498 the south (Fig. 7a), suggesting that the Chupara Fault is likely inactive. Future sampling in the range 499 500 interior and more RSCM data can help to better define the position of the southern extent of the thermal 501 gradient we observe as well as that of the Chupara Fault. We also note that we lack the data needed to 502 speculate whether or how the onshore Chupara Fault relates to any offshore faults (e.g., Robertson and 503 Burke, 1989).

In the southwestern Northern Range, the lower temperature samples of 350–410 °C in the Chancellor schist are separated from the main western block by a fault previously mapped by De Verteuil et al. (2005) (Fig. 7a). This fault may accommodate up to 4 km of vertical slip based on a

typical passive margin geotherm of 25 °C/km (Weber, Ferrill, et al., 2001). The temperature difference 507 between the northwesternmost rocks and the Chancellor schist in the southwest mirrors the S–N grade 508 509 increase observed in Paria, eastern Venezuela by Cruz et al. (2007, and references therein). Two samples ~3–5 km west of the Chupara Fault display slightly lower peak temperatures (~420 °C) than others 510 surrounding them and thus may be separated from the rest of the western block by an additional splay 511 512 fault(s) (e.g., Fig. 3b in Algar & Pindell, 1993) or some other unrecognized fault(s) (Fig. 2; De Verteuil et al., 2005). Finally, one outlier in the west, sample M-4, displays scattered, high peak temperatures of 513 514 497 ± 27 . This sample was collected from a shear zone where processes such as frictional heating during faulting may have altered the CM structure, leading to an increased RSCM-derived temperature 515 (Furuichi et al., 2015). 516

The RSCM results from within the eastern block display an additional, less pronounced, 517 systematic scatter (Fig. 7b), which might reflect second-order gradients or discontinuities that are 518 519 difficult to quantify. This can be seen qualitatively by comparing the CM Raman spectra of samples 520 from the eastern and central Northern Range (following, e.g., Kouketsu et al., 2014). We also note that the increased elongation of quartz grains in central metasandstones indicates a higher degree of quartz 521 ductility and therefore, a potential for deeper burial and higher-grade metamorphism than rocks further 522 523 east (Weber, Ferrill et al., 2001). Furthermore, the Sans Souci metabasalt (Fig. 2) along the northeast coast has a prehnite-pumpellyite mineral assemblage, while the rest of the eastern and central Northern 524 525 Range appears to be mineralogically closer to or within the higher-grade greenschist facies (Frey et al., 526 1988). The RSCM data in the eastern block are sparse, so we are unable to rule out faulting as a cause of 527 the potential eastern thermal gradient, and therefore further work is needed to confirm and more fully quantify the nature of this gradient. 528

529 **6.2** Timing of Metamorphism and Fault-related Exhumation

530	We next used metamorphic ages and low-temperature thermochronology data, together with our
531	RSCM results, to infer the timing of fault slip, differential bedrock cooling, and inferred exhumation
532	along the block-bounding Chupara Fault. Our RSCM data provide new constraints and support for the
533	previously proposed Miocene age of the Northern Range. ⁴⁰ Ar/ ³⁹ Ar spectra from the Northern Range,
534	introduced in abstract form (Foland et al., 1992) and in a field guide (Weber & Arkle, 2015) all indicate
535	ages of ca. 25–30 Ma (Fig. 8b). In addition, Speed et al. (1997) determined the 40 Ar/ 39 Ar age of well-
536	ordered (10Å), syn-metamorphic white mica of the Dragon Gneiss in Paria, Venezuela, presenting an
537	age of 23.3 ± 0.2 Ma (between 8% and 95% Ar release). A second age in that study yielded a total gas
538	age of 34.3 Ma with a plateau around 21 Ma (Speed et al., 1997). We note that the temperature estimates
539	in other geothermometry studies (<400 °C; Frey et al., 1988; Weber, Ferrill, et al., 2001) are all lower
540	than, or close to, the closure temperature of the muscovite ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ system (380 ± 30 °C; Harrison et
541	al., 2009). Because the ⁴⁰ Ar/ ³⁹ Ar ages are mainly taken from metamorphic micas, previous studies
542	regard them as representative of the timing of peak metamorphism. However, some of the younger ages
543	(21-23 Ma) might have experienced Ar loss or resetting during cooling.

544 Zircon fission track (ZFT) data from the Northern Range show a general pattern with reset ages of ~12 Ma in the west (Fig. 8b), whereas most eastern zircons are un-reset and display ages ranging 545 546 from ~80–200 Ma (Algar et al., 1998; Arkle et al., 2021; Weber, Ferrill, et al., 2001). Our new RSCM temperatures from both the east and west (310–450 °C) all exceed the ZFT closure temperature of 240 \pm 547 30 °C (Brandon et al., 1998). This produces some discrepancy because of the presence of detrital ZFT 548 549 ages at these temperatures; this relationship is also seen in studies of Taiwan's mountain ranges (Beyssac 550 et al., 2007; Simoes et al., 2007). These discrepancies are thought to result from the complexities of 551 zircon annealing, including effects related to variable thermal histories and a range of physical and 552 chemical properties of zircon grains (Brandon et al., 1998).

Post-metamorphic thermochronology data from the Northern Range indicate significant 553 differential exhumation of the eastern and western blocks between ~10-4.5 Ma (Arkle et al., 2021), 554 which we suggest corresponds to the period of most active slip of the Chupara Fault (Fig. 8). Arkle et al. 555 (2021) document rapid bedrock cooling and exhumation (~1.5 mm/yr) of the western Northern Range, 556 wherein >7 km of rock was exhumed from $\sim 10-4.5$ Ma (Fig. 8b). During the same time period, thermal 557 558 models indicate that pre-Pliocene exhumation of the eastern Northern Range was only <2 km (Fig. 8a). 559 Although exhumation was clearly focused within the western and eastern crustal blocks of the Northern 560 Range, mechanisms of differential exhumation such as discrete faults or other structures that dissect the 561 mountain range could not previously be identified. We propose that the east-to-west offset of RSCM temperatures we observe need to be consistent with the magnitude and style of offset on the Chupara 562 Fault. The 4 Ma-Recent differential exhumation between the eastern and western Northern Range could 563 be accommodated by faulting, such as reactivation of the Chupara Fault. However, no geomorphic or 564 565 geodetic evidence supports its Quaternary to Recent slip.

566 In the discussions above, we assume that cooling was mainly induced by exhumation. Evidence at the regional scale suggests that a majority of the differential cooling in the Northern Range can most 567 reasonably be attributed to exhumation driven by normal faulting and erosion. Bedrock exhumation by 568 569 erosion off the top of the North Range is supported by the initiation of high sedimentation rates in the Gulf of Paria basin starting at ~4 Ma and in the North Coast basin at ~12 Ma (Flinch et al., 1999). The 570 571 late-stage normal faults pervasive throughout and surrounding the Northern Range (Algar & Pindell, 572 1993; Kugler, 1961; Weber et al., 2015) also indicate favorability for fault-driven exhumation following 573 peak burial. Furthermore, the timing of increased sedimentation, e.g., as described by Flinch et al. (1999), matches the timing of accelerated cooling in the west (late Miocene–Pliocene), suggesting a 574 coupling between sedimentation and bedrock cooling due to erosional exhumation of the Northern 575

Range. On the other hand, Pindell and Kennan (2007) suggest that the underplating of cold proto-576 Caribbean material beneath the western Northern Range is responsible for its cooling (also see 6.3). 577 578 However, this sort of regional-scale thermal conduction would presumably produce a more gradual temperature profile than that seen in our new RSCM data. In addition, such underthrusting is postulated 579 to have occurred before the ~12 Ma Caribbean-South American collision in Trinidad (Algar & Pindell, 580 581 1993; Pindell & Kennan, 2007). If underthrusting did cause significant cooling, its effect should therefore have been strongest before 12 Ma, precluding it from contributing significantly to the younger 582 583 thermal gradient that we observe. Advection of cold fluid can, in principle, also produce steep field gradients (e.g., Rogiers et al., 2014), though its durations are shorter (< 0.1 Myr) and depths are typically 584 much shallower (< 2 km) than the *t*-*T* histories documented herein. 585

586 6.3 Mechanisms of Hinterland Metamorphism

Most models attribute metamorphism and subsequent exhumation of the Northern Range, as well 587 as of Venezuela's Cordillera de la Costa, to the oblique collision between the Caribbean and South 588 American Plates (Algar & Pindell, 1993; Garciacaro et al., 2011; Pindell & Kennan, 2001; Robertson & 589 Burke, 1989). It is also generally agreed upon that exhumation occurred in Trinidad in the mid-Miocene, 590 591 although its mechanism is disputed (Algar & Pindell, 1993; Arkle et al., 2017; 2021; Clark et al., 2008; Cruz et al., 2007; Speed, 1985; Weber, Ferrill, et al., 2001). Our new RSCM temperature estimates 592 exceed temperature estimates from all previous metamorphic studies in the Northern Range (300-350 593 594 °C, Frey et al., 1988; 250–400 °C, Weber, Ferrill, et al., 2001). If attributed to depth, the higher metamorphic grades call for revision of tectonic models to accommodate deep burial; here, we suggest 595 596 that the required deep burial likely occurred through 1) the incorporation of additional shelf sediments 597 into the fold-thrust or accretionary wedge (e.g., Pindell & Kennan, 2001), and 2) transpression acting to

squeeze this material between the two plates, allowing for both increased crustal thickness and orogenicuplift (e.g., Cruz et al., 2007).

600 The Northern Range rocks likely began as a mixture of passive margin (metamorphosed 601 mudstone and turbidites) and continental shelf (becoming marbles and metasandstones) sedimentary protoliths (Fig. 9a). The sequence was incorporated into a fold-thrust wedge along the leading edge of 602 603 the Caribbean plate with varying degrees of transport having been inferred (Fig. 9b; Pindell and Kennan, 604 2001, 2007; Speed, 1985). The two end-members contrasting oblique collision models depict the entire 605 south Caribbean metamorphic hinterland, including the Northern Range, either as an allochthon 606 (Audemard, 2009; Avé Lallemant, 1997; Pindell & Kennan, 2001) or a parautochthon (Cruz et al., 2007; 607 Russo & Speed, 1992, 1994).

608 Tomographic imaging beneath northern South America reveals a sinking mass, which has been associated with either a southward-subducting proto-Caribbean plate (Pindell and Kennan, 2001, 2007) 609 610 or the removal of South American lithosphere along a near vertical crustal STEP (Levandar et al., 2014). The allocthonous model attributes deformation to events occurring since the early Paleocene due to the 611 612 subduction of a proto-Caribbean plate beneath South America. Pindell and Kennan (2007) suggest that 613 the Northern Range represents the accretion of both proto-Caribbean and Caribbean trench sediments. However, no magmatism associated with the southward subduction of a proto-Caribbean lithosphere 614 beneath South America has been found on the South American continent. The lack of upper-plate 615 616 volcanism and differing seismic tomographic interpretations leave the existence of a subducted proto-Caribbean plate open to debate (Levander et al., 2014; Pindell & Kennan, 2001, 2007). In addition, the 617 618 accretionary model (Pindell & Kennan, 2001, 2007) requires about 200 km of displacement since 10 Ma 619 to bring the Northern Range to its current position. This value contrasts with <100 km of displacement 620 along the El Pilar and associated transform plate boundary faults (Audemard, 2009, and references

therein). We also note that the 450 °C temperature from our new RSCM results suggests deeper burial 621 than is typical for both sedimentary and structural burial within accretionary wedges. In addition, the 622 623 lack of high-pressure minerals like sodic-calcic amphiboles and garnet rules out potential high-P/T metamorphism of an oceanic slab such would be expected from the subduction of a large, mature 624 "proto-Caribbean" plate. Thus, we prefer a model with significant crustal shortening associated with 625 626 tectonic burial and crustal downflow to bring the Northern Range protoliths down to depths of ~17 km (25 °C/ km geotherm; c.f. Cruz et al., 2007), although we cannot rule out the possibility of some pre-627 628 collisional influence from a proto-Caribbean plate.

629 Cruz et al. (2007) suggest that the Venezuelan metamorphic belt was exhumed as a two-sided wedge, such as those described in the numerical models of Willet et al. (1993); as the Northern Range 630 represents an extension of this belt, the same mechanism may apply. The geometry of a two-sided 631 wedge (e.g., Cruz et al. 2007) could have been induced in Trinidad by northward subduction of the pre-632 633 collisional oceanic portion of the South American plate beneath the Caribbean plate. The model is 634 supported by the oblique-normal shear indicators and SW-plunging lineations observed in the Cordillera de la Costa, Venezuela (Cruz et al., 2007). In a two-sided wedge, the material is accreted in the foreland 635 and moves towards the retro-wedge of the hinterland, and thus, the metamorphic grade increases 636 637 towards the retro-wedge (Willett et al., 1993). Topographically, a two-sided wedge presents a low-angle taper on the "pro-wedge" portion on the side of the subducting slab, while the "retro-wedge" is on the 638 639 side of the overriding plate and displays a high-angle taper (Willet et al., 1993). The RSCM data from 640 the southwestern Northern Range are consistent with this model, which predicts a metamorphic 641 temperature increase towards the retro-wedge. The Chancellor schist displays lower RSCM temperatures than those in the rest of the western block (340–410 °C, purple unit in Fig. 7a). The range-front position 642 of the Chancellor schist, and the fault-bounded, low-grade Laventille metalimestone and Lopinot 643

644	phyllite (Fig. 2), which display a range-front fold geometry of upright NE-SW trending folds, could
645	reflect the modified southern side of a bivergent wedge (e.g., De Verteuil et al., 2005; Teyssier et al.,
646	2002; Weber, Ferrill, et al. 2001). Farther south in the Central Range, which represents a major foreland
647	fold-thrust structural culmination, <4 km of exhumation occurred from 18–11 Ma (Giorgis et al., 2017).
648	Crustal shortening, development of a deep crustal root, and the deformation of the South American
649	margin (Cruz et al., 2007), likely produced the observed metamorphic grades and significant burial
650	depths of the Northern Range rocks (Fig. 9b). In sum, the lithological, structural, and thermal data of the
651	Northern Range are all consistent with a two-sided wedge model and collision mechanism.
652	The bedrock cooling models of Arkle et al. (2021) indicate that a significant amount of post-
653	collisional cooling and exhumation occurred in the western Northern Range from ~10-4.5 Ma, while
654	little cooling and exhumation occurred in the east during that same time period. Arkle et al. (2021)
655	further speculate that the STEP edge passed eastward under Trinidad following oblique collision (Fig.
656	9c), creating a series of late-stage, en echelon normal faults that accommodated the overall strike-slip
657	(transform) motion that is also pervasive throughout the Northern Rin Trinidad (Algar & Pindell, 1993;
658	De Verteuil et al., 2005) and eastern Venezuela (Cruz et al., 2007). We propose that the Chupara Fault
659	may be such a post-orogenic, extensional feature (Figs. 2, 7a, 9c). Thus, the activity of the Chupara
660	Fault may be linked to the exhumation of the deeply buried rock in the western Northern Range that we
661	document using RSCM data, perhaps as the STEP front migrated eastward (Fig. 9c). Thermal models,
662	erosion data, and other regional geomorphic data also indicate that differential cooling and exhumation
663	inverted around 4.5 Ma (Arkle et al., 2017: 2021). The STEP edge at this time (~4.5 Ma) would have
664	moved sufficiently far to the east, became insignificant in the Northern Range, and brought the activity
665	along the Chupara Fault to an end (Fig. 9d).

7. CONCLUSIONS

RSCM geothermometry provides important constraints on the peak metamorphic temperatures of 667 668 key lithologic units across the Northern Range and helps to fill vital gaps in our understanding of its 669 thermal history. The RSCM data collected across a broad swath of the range reveals a discrete thermal gradient with peak metamorphic temperatures of 337 ± 10 °C in the east and 442 ± 16 °C in the west, 670 confirming the field gradient proposed by Frey et al. (1988) and demonstrated by Weber, Ferrill, et al. 671 672 (2001). The abrupt temperature discontinuity of $105 \pm 19^{\circ}$ C located at Chupara Point corresponds to the 673 location of the previously mapped Chupara Fault. Further field work is required to better constrain the 674 precise location, timing, and kinematics of the Chupara Fault. Our new RSCM temperature estimates 675 surpass all previous estimates and thus require greater burial depths of Northern Range rock. We speculate that Miocene oblique plate motion created a two-sided wedge in which parautochthonous 676 Northern Range rocks were incorporated into a fold-thrust hinterland wedge. Our new peak 677 temperatures, together with thermochronological data, lead us to interpret that the Chupara Fault is 678 679 likely the main structure that accommodated differential exhumation between the eastern and western 680 Northern Range. The distinctly different cooling trajectories suggest that the Chupara Fault was likely active from ~10–4.5 Ma, though activity before or after this time period cannot be completely ruled out. 681

682 Acknowledgments

This study was inspired by a departmental field trip to the Caribbean, organized and led by Professor Emeritus Edward Spooner and Laurent de Verteuil, along with undergraduate students Colin Roth and Jason Hinde. The Raman analyses and training at the University of Turin were supported by an Undergraduate Student Research Award of the Natural Sciences and Engineering Research Council (NSERC USRA, reference number 501984) to I.G. and a MIUR grant Levi Montalcini to A.V.B. The study is also supported by NSERC (Discovery Grant RGPIN-2018-03925 to X.C.). This work is part of a project that has received funding from the European Research Council (ERC) under the European 690 Union's Horizon 2020 research and innovation programme (Grant agreement No. 864045). We thank

691 Veronica DiCecco and Yanan Liu for help with Raman spectroscopy and the electron microprobe

analysis, at the Royal Ontario Museum and the University of Toronto respectively. Sample collection by

- 693 Adam Brudner is gratefully acknowledged.
- 694
- 695
- 696
- 697 **References**
- Algar, S. T., & Pindell, J. L. (1993). Structure and deformation history of the Northern Range of
 Trinidad and adjacent areas. *Tectonics*, 12(4), 814–829. https://doi.org/10.1029/93TC00673
- Algar., S. T., Heady, E. C., & Pindell, J. L. (1998). Fission-track dating in Trinidad: Implications for
- 701 provenance, depositional timing and tectonic uplift. In Pindell, J. L., & Drake, C. (Eds.),
- 702 Paleogeographic evolution and non-glacial eustasy, northern South America (Special Publication 58,
- pp. 111–128). Tulsa, OK: Society of Economic Paleontologists and Mineralogists.
- Anovitz, L. M., & Essene, E. J. (1987). Phase Equilibria in the System CaCO3-MgCO3-FeCO3.
 Petrology, 28(2), 389–414. https://doi.org/10.2473/shigentosozai1953.98.1131_441
- Aoya, M., Kouketsu, Y., Endo, S., Shimizu, H., Mizukami, T., Nakamura, D., & Wallis, S. (2010).
- 707 Extending the applicability of the Raman carbonaceous-material geothermometer using data from
- contact metamorphic rocks. Journal of Metamorphic Geology, 28, 895–914.
- 709 https://doi.org/10.1111/j.1525-1314.2010.00896.x
- 710 Arkle, J. C., Owen, L. A., Weber, J. C., Caffee, M. W., & Hammer, S. (2017). Transient Quaternary
- erosion and tectonic inversion of the Northern Range, Trinidad. *Geomorphology*, 295, 337–353.
 https://doi.org/10.1016/j.geomorph.2017.07.013
- 713 Arkle, J. C., Weber, J. C., Enkleman, E., Owen, L. A., Govers, R., Denison, C., et al. (2021).
- Exhumation of the coastal metamorphic belt above a subduction-to-transform transition, in the southeast
- 715 Caribbean plate corner. *Tectonics*, 40(8). https://doi.org/10.1029/2020TC006414
- Audemard, F. A. (2009). Key issues on the post-Mesozoic Southern Caribbean Plate boundary.
 Geological Society Special Publication, 328, 569–586. https://doi.org/10.1144/SP328.23
- 718 Avé Lallemant, H. G. (1997). Transpression, displacement partitioning, and exhumation in the eaastern
- 719 Caribbean / South American plate boundary zone. *Tectonics*, 16(2), 272–289.
- 720 http://dx.doi.org/10.1029/96TC03725
- Babb, S. and Mann, P. (1999). Structural and sedimentary development of a Neogene transpressional
- 722 plate boundary between the Caribbean and South American plates in Trinidad and the Gulf of Paria. In

- Mann, P., ed., *Caribbean basins: Sedimentary basins of the world* (Volume 4, pp. 495–557).
- 724 Amsterdam, Netherlands: Elsevier Science B.V.
- Barr, K.W. (1965). The Geology of the Toco District, Trinidad, West Indies, Pt. I and II. Overseas
 Geology and Mineral resources, 8, 4, 379-415 and 9, 1, 1-29.
- Bartlett, C., Arkle, J., Weber, J. and Erlich, R. (2021). Provenance of the Northern Range Trinidad
- 728 Using Detrital Zircon U-Pb Geochronology: Implications for Northern South American River System
- 729 Paleogeography, Geological Society of America, North-Central Meeting.
- Bayet, L., John, T., Agard, P., Gao, J., & Li, J. (2018). Massive sediment accretion at ~80 km depth
 along the subduction interface: Evidence from the southern Chinese Tianshan. *Geology*, 46(6), 495–498.
 https://doi.org/10.1130/G40201.1
- 733 Beyssac, O., Goffé, B., Chopin, C., & Rouzaud, J. N. (2002). Raman spectra of carbonaceous material in
- metasediments: a new geothermometer. *Journal of Metamorphic Geology*, 20, 859–871.
 https://doi.org/10.1046/j.1525-1314.2002.00408.x
- 736 Beyssac, O., Goffé, B., Petitet, J. P., Froigneux, E., Moreau, M., & Rouzaud, J. N. (2003). On the
- rise beyssae, o., cone, b., renter, s. r., rorgheax, E., whereau, m., et Rouzaud, s. R. (2005). On the rise characterization of disordered and heterogeneous carbonaceous materials by Raman spectroscopy.
- 738 Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 59, 2267–2276.
- 739 https://doi.org/10.1016/S1386-1425(03)00070-2
- Beyssac, O., & Lazzeri, M. (2012). Application of raman spectroscopy to the study of graphitic carbons
 in the earth sciences. *European Mineralogical Union Notes in Mineralogy*, 12(12), 415–454.
- 742 https://doi.org/10.1180/EMU-notes.12.12
- 743 Beyssac, O., Pattison, D. R. M., & Bourdelle, F. (2019). Contrasting degrees of recrystallization of
- carbonaceous material in the Nelson aureole, British Columbia and Ballachulish aureole, Scotland, with
 implications for thermometry based on Raman spectroscopy of carbonaceous material. *Journal of*
- 746 *Metamorphic Geology*, 37, 71–95. https://doi.org/10.1111/jmg.12449
- 747 Beyssac, O., Simoes, M., Avouac, J. P., Farley, K. A., Chen, Y. G., Chan, Y. C., & Goffé, B. (2007).
- Late Cenozoic metamorphic evolution and exhumation of Taiwan. Tectonics, 26(6).
- 749 https://doi.org/10.1029/2006TC002064
- 750 Brandon, M. T., Roden-Tice, M. K., & Carver, J. I. (1998). Late Cenozoic exhumation of the Cascadia
- accretionary wedge in the Olympic Mountains, northwest Washington State. *Bulletin of the Geological Society of America*, 110(8), 985–1009. https://doi.org/10.1130/0016-
- 753 7606(1998)110<0985:LCEOTC>2.3.CO;2
- Burke, K. (1988). Tectonic evolution of The Caribbean. *Annual Reviews in Eath and Planetary Science*,
 16, 201–230. https://doi.org/10.1146/annurev.ea.16.050188.001221
- 756 Clark, S. A., Sobiesiak, M., Zelt, C. A., Magnani, M. B., Miller, M. S., Bezada, M. J., & Levander, A.
- 757 (2008). Identification and tectonic implications of a tear in the South American plate at the southern end
- of the Lesser Antilles. *Geochemistry, Geophysics, Geosystems*, 9(11), 1–10.
- 759 https://doi.org/10.1029/2008GC002084

- 760 Cruz, L., Fayon, A., Teyssier, C., & Weber, J. C. (2007). Exhumation and deformation processes in
- transpressional orogens: The Venezuelan Paria Peninsula, SE Caribbean-South American plate
- boundary. *Special Paper of the Geological Society of America*, 434(8), 149–165.
- 763 https://doi.org/10.1130/2007.2434(08)
- 764 De Verteuil, L., Weber, J. C., Ramlal, B., & Gonzalez Alfonso, J. A. (2005). Geological Map of
- 765 *Trinidad*. Republic of Trinidad and Tobago: Latinum Geological Consultants Limited.
- Dighton-Thomas, H. (1935). On some sponges and a coral of Upper Cretaceous Age from Toco Bay,
 Trinidad, Geological Magazine, 72, 4, 175-179.
- 768
- Flinch, J. F., Rambaran, V., Ali, W., De Lisa, V. De, Hernández, G., Rodrigues, K., & Sams, R. (1999).
- 770 Structure of the Gulf of paria pull-apart basin (Eastern Venezuela-Trinidad). In Mann, P., (Ed.)
- 771 Sedimentary Basins of the World (Vol. 4, pp. 477–494). Frisco CO: Elsevier Science.
- 772 https://doi.org/10.1016/S1874-5997(99)80051-3
- Foland, K. A., Speed, R., & Weber, J. C. (1992). Geochronologic studies of the hinterland of the
 Caribbean orogen of Venezuela and Trinidad. *Geological Society of America Abstracts with Programs*,
- 775 24, 148.
- Furuichi, H., Ujiie, K., Kouketsu, Y., Saito, T., Tsutsumi, A., Wallis, S. (2015). Vitrinite reflectance and
- 777 Raman spectra of carbonaceous material as indicators of frictional heating on faults: Constraints from
- friction experiments. *Earth and Planetary Letters*, 424, 191–200.
- 779 https://doi.org/10.1016/j.epsl.2015.05.037
- Frey, M., Saunders, J., & Schwander, H. (1988). The mineralogy and metamorphic geology of low-
- grade metasediments, Northern Range, Trinidad. *Journal of the Geological Society, London*, 145, 563–
 575. https://doi.org/10.1144/gsjgs.145.4.0563
- Garciacaro, E., Mann, P., & Escalona, A. (2011). Regional structure and tectonic history of the obliquely
 colliding Columbus foreland basin, offshore Trinidad and Venezuela. *Marine and Petroleum Geology*,
 28, 126–148. https://doi.org/10.1016/j.marpetgeo.2009.08.016
- Gennaro, I., Chu, X., Vitale Brovarone, A., Weber, J., Arkle, J. (2021). Peak metamorphic temperatures
 aquired through Raman Spectroscopy on Carbonaceous Material (RSCM) from the Northern Range,
 Trinidad. PANGAEA, https://doi.pangaea.de/10.1594/PANGAEA.932772
- Giorgis, S., Weber, J. C., Sanguinito, S., Beno, C., & Metcalf, J. (2017). Thermochronology constraints
 on miocene exhumation in the central range mountains, Trinidad. *Bulletin of the Geological Society of America*, 129(1–2), 171–178. https://doi.org/10.1130/B31363.1
- Govers, R., & Wortel, M. J. R. (2005). Lithosphere tearing at STEP faults: Response to edges of
 subduction zones. Earth and Planetary Science Letters, 236(1–2), 505–523.
 https://doi.org/10.1016/j.apsl.2005.03.022
- 794 https://doi.org/10.1016/j.epsl.2005.03.022
- Harrison, T. M., Célérier, J., Aikman, A. B., Hermann, J., & Heizler, M. T. (2009). Diffusion of 40Ar in
- muscovite. *Geochimica et Cosmochimica Acta*, 73(4), 1039–1051.
- 797 https://doi.org/10.1016/j.gca.2008.09.038
- Hoernle, K., Hauff, F., & van den Bogaard, P. (2004). 70 m.y. history (139-69 Ma) for the Caribbean
 large igneous province. *Geology*, 32(8), 697–700. https://doi.org/10.1130/G20574.1

- Imlay, R.W. (1954). Barremian ammonites from Trinidad, B.W.I., Journal of Paleontology, 28, 5, 662667.
- Iwasaki, R., Hirose, M., & Furukawa, Y. (2013). Raman temperature measurements of copper
 phthalocyanine layer of organic light-emitting diode using bandwidth-temperature relationship.
- *Japanese Journal of Applied Physics*, 52(5S1), 05DC16.
- Kagi, H., Tsuchida, I., Wakatsuki, M., Takahashi, K., Kamimura, N., Iuchi, K., & Wada, H. (1994).
- 806 Proper understanding of down-shifted Raman spectra of natural graphite: Direct estimation of laser-
- induced rise in sample temperature. *Geochimica et Cosmochimica Acta*, 58(16), 3527-3530.
- Kirlova, M., Toy, V., Rooney, J. S., Giorgetti, C., Gordon, K. C., Collettini, C., Takeshita, T. (2018).
 Structural disorder of graphite and implications for graphite thermometry. *Solid Earth*, 9, 223–231.
 https://doi.org/10.5194/se-9-223-2018
- 811 Kugler, H. G. (1961). *Geological map and sections of Trinidad*. Zurich, Switzerland: Orell Füssli Arts
- 812 Graphiques S. A.
- Kennan, L., & Pindell, J. L. (2009). Dextral shear, terrane accretion and basin formation in the Northern
 Andes: Best explained by interaction with a Pacific-derived Caribbean plate? *Geological Society Special*
- 815 *Publication*, 328, 487–531. https://doi.org/10.1144/SP328.20
- Kouketsu, Y., Mizukami, T., Mori, H., Endo, S., Aoya, M., Hara, H., et al. (2014). A new approach to
 develop the Raman carbonaceous material geothermometer for low-grade metamorphism using peak
 width. *Island Arc*, 23, 33–50. https://doi.org/10.1111/iar.12057
- Lahfid, A., Beyssac, O., Deville, E., Negro, F., Chopin, C., & Goffé, B. (2010). Evolution of the Raman
 spectrum of carbonaceous material in low-grade metasediments of the Glarus Alps (Switzerland). *Terra Nova*, 22(5), 354–360. https://doi.org/10.1111/j.1365-3121.2010.00956.x
- 822 Levander, A., Bezada, M. J., Niu, F., Humphreys, E. D., Palomeras, I., Thurner, S. M., et al. (2014).
- 823 Subduction-driven recycling of continental margin lithosphere. *Nature*, 515, 253–256.
- 824 https://doi.org/10.1038/nature13878
- Lünsdorf, N. K., Dunkl, I., Schmidt, B. C., Rantitsch, G., & von Eynatten, H. (2013). Towards a Higher
- 826 Comparability of Geothermometric Data obtained by Raman Spectroscopy of Carbonaceous Material.
- Part I: Evaluation of Biasing Factors. *Geostandards and Geoanalytical Research*, 38(1), 73–94.
- 828 https://doi.org/10.1111/j.1751-908X.2013.12011.x
- Luque, F. J., Pasteris, J. D., Wopenka, B., Rodas, M., & Barrenechea, J. F. (1998). Natural Fluid-
- Biggin Deposited Graphite: Mineralogical Characteristics and Mechanisms of Formation. *American Journal of Science*, 298(6), 471–498. https://doi.org/10.2475/ajs.298.6.471
- Molli, G., Vitale Brovarone, A., Beyssac, O., & Cinquini, I. (2018). RSCM thermometry in the Alpi
- Apuane (NW Tuscany, Italy): New constraints for the metamorphic and tectonic history of the inner northern Apennines. *Journal of Structural Geology*, 113, 200–216.
- 834 northern Apennines. *Journal of Structural Geology*, 1
 835 https://doi.org/10.1016/j.jsg.2018.05.020
- 836 Nakamura, Y., Hara, H., & Kagi, H. (2019). Natural and experimental structural evolution of dispersed
- organic matter in mudstones: The Shimanto accretionary complex, southwest Japan. *Island Arc*, 28(5),
 e12318.

- 839 Nakamura, Y., Oohashi, K., Toyoshima, T., Satish-Kumar, M., Akai, J. (2015). Strain-induced
- amorphization of graphite in fault zones of the Hidaka metamorphic belt, Hokkaido, Japan. *Journal of Structural Geology*, 72, 142–161. https://doi.org/10.1016/j.jsg.2014.10.012
- Neill, I., Kerr, A., Chamberlain, K. R., Schmitt, A. K., Urbani, F., Hastie, A. R. et al. (2014). Vestiges of
 the proto-Caribbean seaway: Origin of the Sans Souci volcanic group, Trinidad. *Tectonophysics*, 626,
 170–185. https://doi.org/10.1016/j.tecto.2014.04.019
- 245 Nilheld N & Course D (2015) The selection requires an the coulottic
- Nijholt, N., & Govers, R. (2015). The role of passive margins on the evolution of Subduction-Transform
 Edge Propagators (STEPs). *Journal of Geophysical Research: Solid Earth*, 120, 7203–7230.
- 847 https://doi.org/10.1002/2015JB012202
- Pindell, J., & Kennan, L. (2001). Processes and Events in the Terrane Assembly of Trinidad and Eastern
 Venezuela. In *Petroleum Systems of Deep-Water Basins: Global and Gulf of Mexico Experience: 21st*
- Annual (159–192). Red Hook, NY: Curran Associates Inc. https://doi.org/10.5724/gcs.01.21.0159
- 851 Pindell, J. & Kennan, L. (2007). Cenozoic Kinematics and Dynamics of Oblique Collision Between two
- 852 Convergent Plate Margins: The Caribbean-South America Collision in Eastern Venezuela, Trinidad and
- Barbados. In Transactions of GCSSEPM 27th Annual Bob F. Perkins Research Conference, 458-553.
- 854 https://doi.org/10.5724/gcs.07.27.0458
- Pindell, J. & Kennan, L. (2009). Tectonic evolution of the Gulf of Mexico, Caribbean and northern
- 856 South America in the mantle reference frame: an update. In *Geological Society London, Special* 857 *Publications* 328 1 55 https://doi.org/10.1144/SP328.1
- 857 *Publications*, 328, 1–55. https://doi.org/10.1144/SP328.1
- Potter, H. C. (1968). A preliminary account of the stratigraphy and structure of the eastern part of the
 Northern Range, Trinidad. In *Transactions of the Fourth Caribbean Geological Conference*, Trinidad,
 15–20.
- Potter, H. C. (1973). The overturned anticline of the Northern Range of Trinidad near Port of Spain. *Journal of the Geological Society*, 129, 133–137. http://dx.doi.org/10.1144/gsjgs.129.2.0133
- Rahl, J. M., Anderson, K. M., Brandon, M. T., & Fassoulas, C. (2005). Raman spectroscopic
- carbonaceous material thermometry of low-grade metamorphic rocks: Calibration and application to
 tectonic exhumation in Crete, Greece. *Earth and Planetary Science Letters*, 240(2), 339–354.
- 866 https://doi.org/10.1016/j.epsl.2005.09.055
- Robertson, P., & Burke, K. (1989). Evolution of southern Caribbean plate boundary, vicinity of Trinidad
 and Tobago. *American Association of Petroleum Geologists Bulletin*, 73(4), 490–509.
 https://doi.org/10.1306/44b49fdd-170a-11d7-8645000102c1865d
- 870 Rogiers, B., Huysmans, M., Vandenberghe, N., Verkeyn, M. (2014). Demonstrating large-scale cooling
- in a Variscan terrane by coupled groundwater and heat flow modelling. *Geothermics*, 51, 71–90.
- 872 http://dx.doi.org/10.1016/j.geothermics.2013.10.014
- 873 Rumble, D. (2014). Hydrothermal graphitic carbon. *Elements*, 10(6), 427–433.
- 874 https://doi.org/10.2113/gselements.10.6.427
- 875 Russo, R. M., & Speed, R. C. (1992). Oblique collision and tectonic wedging of the South American
- continent and Caribbean terranes. *Geology*, 20(5), 447–450. https://doi.org/10.1130/0091-
- 877 7613(1992)020<0447:OCATWO>2.3.CO;2

- 878 Russo, R. M., & Speed, R. C. (1994). Spectral analysis of gravity anomalies and the architecture of
- tectonic wedging, NE Venezuela and Trinidad. *Tectonics*, 13(3), 613–622.
- 880 https://doi.org/10.1029/94TC00052
- Simoes, M., Avouac, J. P., Beyssac, O., Goffé, B., Farley, K. A., & Chen, Y. G. (2007). Mountain
- building in Taiwan: A thermokinematic model. *Journal of Geophysical Research: Solid Earth*, 112(11),
 1–25. https://doi.org/10.1029/2006JB004824
- Saunders, J.B. (1972). Recent paleontological results from the Norther Range of Trinidad, Proceedings
 on the Sixth Caribbean Geological Conference, Caracas, 455-460.
- Saunders, J. B., Roberts, C., Ali, W. M., Eggerston, B. (1997). *Geological Map, Trinidad and Tobago*.
 Trinidad and Tobago: Ministry of Energy and Energy Resources.
- Spath, L.F. (1939). On some Tithonian ammonites from the Northern Range of Trinidad, British West
 Indies Geological Magazine, 76, 898, 187-198.
- Speed, R. C. (1985). Cenozoic Collision of the Lesser Antilles Arc and Continental South America and
 the Origin of the El Pilar Fault. *Tectonics*, 4(1), 41–69. https://doi.org/10.1029/TC004i001p00041
- Speed, R.C., Sharp, W.D., and Foland, K.A., (1997). Late Paleozoic granitiod gneiss of northeastern
 Venezuela and the North American-Gondwana collision zone, Journal of Geology, 105(4), 457–470.
- Teyssier, C., Tikoff, B., Weber, J. (2002). Attachment between brittle and ductile crust at wrenching
 plate boundaries. *EGU Stephan Mueller Special Publication Series*, 1, 75–91.
- Trechmann, C.T. (1935). Fossils from the Northern Range of Trinidad, Geological Magazine, 72, 850,
 166-175.
- 898 Vitale Brovarone, A., & Agard, P. (2013). True metamorphic isograds or tectonically sliced
- metamorphic sequence? New high-spatial resolution petrological data for the New Caledonia case study.
 Contributions to Mineralogy and Petrology, 166(2), 451–469. https://doi.org/10.1007/s00410-013-0885 2
- Vitale Brovarone, A., Beyssac, O., Malavieille, J., Molli, G., Beltrando, M., & Compagnoni, R. (2013).
- 903 Stacking and metamorphism of continuous segments of subducted lithosphere in a high-pressure wedge:
- The example of Alpine Corsica (France). *Earth-Science Reviews*, 116(1), 35–56.
- 905 https://doi.org/10.1016/j.earscirev.2012.10.003
- Wadge, G & Macdonald, R. (1985). Cretaceous tholeiites of the southern continental margin of South
 America: the Sans Souci Formation of Trinidad. *Journal of the Geological Society of London*, 142, 297–
 308. https://doi.org/10.1144/gsjgs.142.2.0297
- Wang, Y., Alsmeyer, D. C., McCreery, R. L. (1990). Raman spectroscopy of carbon materials:
 Structural basis of observed spectra. *Chemical Materials*, 2, 557–563.
- Weber, J. C. (2009). Neotectonics in the Trinidad and Tobago, West Indies segment of the CaribbeanSouth American plate boundary. *Occasional Papers of the Geological Institute of Hungary*, 204, 21–29.
- 913 Weber, J. C., & Arkle, J. (2015). *Field Trip Field Guide Trinidad's Northern Range: "reversal of*
- 914 fortune": Bedrock Structure and Metamorphic Geology, and Tectonic Geomorphology. Port-of-Spain,
- 915 Trinidad: 20th Caribbean Geological Conference.

- 916 Weber, J. C., Dixon, T. H., DeMets, C., Ambeh, W. B., Jansma, P., Mattioli, G., et al. (2001). GPS
- estimate of relative motion between the Caribbean and South American plates, and geologic
- 918 implications for Trinidad and Venezuela. *Geology*, 29(1), 75–78. https://doi.org/10.1130/0091-
- 919 7613(2001)029<0075:GEORMB>2.0.CO;2
- 920 Weber, J. C., Ferrill, D. A., & Roden-Tice, M. K. (2001). Calcite and quartz microstructural
- geothermometry of low-grade metasedimentary rocks, Northern Range, Trinidad. Journal of Structural
- 922 Geology, 23(1), 93–112. https://doi.org/10.1016/S0191-8141(00)00066-3
- 923 Weber, J. C., H. Geirsson, J. L. Latchman, K. Shaw, P. La Femina, S. Wdowinski, M. Higgins, C.
- 924 Churches, and E. Norabuena (2015), Tectonic inversion in the Caribbean-South American plate
- boundary: GPS geodesy, seismology, and tectonics of the M_W 6.7 22 April 1997 Tobago earthquake,
- 926 Tectonics, 34, 1181–1194, doi:10.1002/2014TC003665.
- 927 Weber, J. C., Geirsson, H., La Femina, P., Robertson, R., Churches, C., Shaw, K., et al. (2020). Fault
- 928 Creep and Strain Partitioning in Trinidad-Tobago: Geodetic Measurements, Models, and Origin of
- 929 Creep. *Tectonics*, 39(1), e2019TC005530. https://doi.org/10.1029/2019TC005530
- 930 Willett, S., Beaumont, C., & Fullsack, P. (1993). Mechanical model for the tectonics of doubly vergent
- 931 compressional orogens. *Geology*, 21(4), 371–374. https://doi.org/10.1130/0091-
- 932 7613(1993)021<0371:MMFTTO>2.3.CO;2
- Wopenka, B., & Pasteris, J. D. (1993). Structural characterization of kerogens to granulite-facies
- graphite: Applicability of Raman microprobe spectroscopy. American Mineralogist, 78(5–6), 533–557.
- 935
- 936

Sample	Spectro- meter	Lithology	UTM X coordinate ^a	UTM Y coordinate ^a	5-Peak S Tempe (SE	Spectra rature E) ^f	3-Peak Spectra Temperature (SE) ^g		RSCM Temperature (SE) ^e		FWHM-D1 Temperature (SE) ^h		FWHM-D2 Temperature (SE) ^h	
DT-93-1 ^b	-	Phyllite	672200	1189900	-	-	-	-	-	-	-	-	-	-
145	UNITO	Schist	672500	1178400			348	2.9	348	2.9	362	3.6	277	18.3
HT-161	ROM	Phyllite	672500	1178400	341	4.0	355	2.1	347	4.7	360	3.4	383	3.6
CF-94-1	ROM	Marble	672698	1178373			353	1.8	353	1.8	367	2.6	332	6.8
T94-3	ROM	Slate	723638	1198298	325	4.4			325	4.4	287	5.0	320	1.1
T97- MAT3	ROM	Slate	706235	1196714	339	2.9			339	2.9	298	2.1	322	0.9
M-3	UNITO	Schist	671697	1189674	1 out	tlier	461	4.7	461	4.7	-	-	-	-
	ROM	Schist	671697	1189674			447	3.6	447	3.6	-	-	-	-
	UNITO	Schist	671697	1189674	l out	tlier	497	7.9	497	7.9	-	-	-	-
IVI-4	ROM	Schist	671697	1189674			492	10.6	492	10.6	-	-	-	-
Ar-17	ROM	Metasandstone	683682	1193264	364	3.9			364	3.9	334	3.5	310	3.6
LC-91a	UNITO	Metasandstone	675697	1192174			413	3.6	413	3.6	-	-	-	-
T90-9b	ROM	Phyllite	672820	1178826			340	1.4	340	1.4	354	3.1	298	7.1
LN-94-1	UNITO	Metacarbonate	721934	1197921	327	3.1			327	3.1	243	5.3	256	11.7
	ROM	Metacarbonate	721934	1197921	272	3.5			272	3.5	270	5.8	292	9.1
SC-2	UNITO	Marble	666223	1185430			465	8.6	465	8.6	-	-	-	-
T94-1	UNITO	Metacarbonate	723497	1198074	322	2.7			322	2.7	227	7.9	323	5.5
194-1	ROM	Metacarbonate	723497	1198074	302	2.5			302	2.5	245	3.5	360	3.5
SC-2b	UNITO	Marble	669482	1189870	1 out	tlier	449	4.1	449	4.1	-	-	-	-
MV-94-3	ROM	Metacarbonate	717297	1197675	310	3.5			310	3.5	263	1.6	319	7.2
PG-94-5°	ROM	Metacarbonate	650597	1180273			315 ^c		315°		314 ^c		287°	
93-T-CB	UNITO	Marble	679302	1194346	3 out	liers	366	4.6	366	4.6	354	2.4	248	8.9
MAT-1	ROM	Slate	704866	1196982	341	4.1	1 ou	tlier	341	4.1	292	3.2	320	3.7
CD 2	UNITO	Marble	678698	1195474	348 ^d		344	1.2	344	1.2	349	2.1	233	10.9
CD-2a	ROM	Marble	678698	1195474			341	1.4	341	1.4	366	2.3	302	5.8
DT 02	UNITO	Schist	672763	1189887			454	2.9	454	2.9	-	-	-	-
D1-93	ROM	Schist	672763	1189887			453	3.3	453	3.3	-	-	-	-
MB-93-1	ROM	Schist	650900	1187570			444	5.2	444	5.2	-	-	-	-
LC-91b	UNITO	Schist	676033	1192116			422	3.9	422	3.9	-	-	-	-
LC-3	ROM	Phyllite	661869	1180984			410	2.2	410	2.2	-	-	-	-
ND 1	UNITO	Metasandstone	720092	1185918			338	0.3	337	2.2	343	2.0	244	7.2
INK-1	ROM	Metasandstone	720092	1185918	336	4	341	1.1	342	1.1	355	1.5	287	3.8
NR-2 (-5)	UNITO	Slate	724652	1192884	351	1.5	340	***	350	4.5	311	1.9	311	4.1
NR-3 (-1)	UNITO	Metasandstone	720092	1185918	327	1.3	335	0.3	329	3.7	318	5.5	174	10.8

937 <u>Table 1. Rock Type, Location, and RSCM Temperatures of Northern Range Samples</u>

- 939 ^a UTM coordinates are in Zone 20.
- 940 ^b Sample DT-93-1 was unable to be analyzed due to a lack of carbonaceous material.
- Sample PG-94-5 has a temperature based on one spectrum as all other spectra collected contained large calcite peaks and could
 not be fit accurately.
- 943 ^d One spectrum only.
- ^e These temperatures are calculated using the Aoya et al. (2010) or Lahfid et al. (2010) calibrations. In samples displaying both 3-
- and 5-band spectra both calibrations were used, with the reported value representing the average temperature of all spectra
- associated with that sample (exculding outliers). Consult the supplementary material for a full breakdown of the calibrations used
- 947 for each spectrum.
- 948 ^f Aoya et al. (2010).
- 949 ^g Lahfid et al. (2010).
- 950 ^h Kouketsu et al. (2014).

951 Figure Captions

952

Figure 1: a) Schematic tectonic map of the eastern Caribbean showing major plate boundaries. Trinidad 953 (grey) is currently located on the right-lateral strike-slip transform boundary along the southern edge of 954 955 the Caribbean Plate. PC – Paria cluster of seismicity. b) Map of Trinidad emphasizing the Northern Range study area (grey) and major faults in the region. The active faults (Central Range and Los Bajos 956 957 faults, bold lines) accommodate most of the present plate motion between the Caribbean and South 958 America (Weber, Dixon, et al., 2001). The Northern Range is bound by the inactive North Coast and 959 Sub-Tobago Terrane fault zones to the north and Arima Fault to the south. The El Pilar Fault zone is 960 active in eastern Venezuela but is inactive or not present in Trinidad. c) Cross section of the subduction-961 transform edge propagator (STEP) plate boundary and associated lithospheric tear located below the Caribbean Plate. The subduction-transform boundary is located at the letter "S" while the site of active 962 963 and deep tearing is located at the Paia Cluster, which is a major zone of earthquakes in the area as a 964 result of the slab tear (Russo & Speed, 1992). Modified after Arkle et al. (2021).

965

974

966 Figure 2: Simplified geologic map from De Verteuil et al. (2005) of the Northern Range showing metamorphic units, sample localities, and relict fossil ages. Apart from the Sans Souci Metabasalt, all 967 lithologic units are metamorphosed from sedimentary protoliths (Frey et al., 1988), with relict fossil 968 ages only available from eastern block, lower-grade units (Dighton-Thomas, 1935; Imlay, 1954; Kugler, 969 970 1961; Saunders, 1972; Spath, 1939; Trechmann, 1935). A total of 26 RSCM samples were collected and grouped into six representative rock types. Sample distribution was based on obtaining a broad range of 971 compositions and textures. PS - Port of Spain; CP - Chupara Point; VV - Verdant Vale; M - Maturita; 972 973 T – Toco.

975 Figure 3: Photomicrographs of petrographic thin sections displaying representative features of each rock type. a) calcite (Cal) marble with carbonaceous material (Gr) concentrated into dark bands; b) 976 calcite (Cal) vein in a metacarbonate rock indicating late extensional brittle deformation and infilling via 977 precipitation from a CO₂-rich fluid; c) low-grade metacarbonate marble displaying primary sedimentary 978 979 structures (ooids) which have been moderately strained by ductile deformation but have not been recrystallized; d) quartz-mica (Qz-Ms) schist with foliation and minor calcite, likely representing a 980 sandstone protolith; e) mica-rich (Ms) phyllite displaying crenulation after multiple deformation events; 981 f) radial growth of carbonaceous material (CM) superimposed on schistosity; g) metasandstone with 982 minor chlorite (Chl), muscovite, and quartz (Qz); h) folded quartz (Qz)- and CM (Gr)-rich layers in a 983 metasandstone; i) slate rich in carbonaceous material, quartz (Qz), and mica (Ms). PPL: plane-polarized 984 light, XPL: cross-polarized light, RL: reflected light. 985

986

Figure 4: a) Backscattered electron (BSE) image of a foliated slate. The dolomite (dol) in the sample
has a euhedral shape whereas the calcite (cc) appears more subhedral-anhedral, indicating a lack of
equilibrium between the two phases. Pyrite (py) framboids are also present. b) CaCO₃-MgCO₃-FeCO₃

phase diagrams calculated for different temperatures (Anovitz & Essene, 1987), with carbonate

- 991 compositions plotted in red.
- 992

Figure 5: Peak-fitted Raman spectra of (a) high- and (b) low- temperature samples. The hightemperature spectra are fit with Voigt bands while Lorentzian bands are used for the low-temperature
spectrum; the area ratios between these bands are used to calculate the peak metamorphic temperature of
a sample (Aoya et al., 2010; Lahfid et al., 2010). c) Raman spectra showing decreasing band complexity,
correlating to increasing crystallinity and peak metamorphic temperature, from bottom to top. The
temperatures shown are calculated using the ¹Lahfid et al. (2010) and ²Aoya et al. (2010) calibrations.

999

Figure 6: Inter-instrument error between Raman spectrometers at UNITO and the ROM. The lowtemperature calibrations of Lahfid et al. (2010) and Kouketsu et al. (2014) show a lower reproducibility
than the high-temperature calibration of Aoya et al. (2010). Inset: variability between the two

1003 calibrations of Kouketsu et al. (2014) which are up to $100 \,^{\circ}$ C.

1004

Figure 7: a) RSCM results given in °C plotted on a geologic map of Trinidad overlying topographic 1005 (radar) data. The abrupt temperature change in the central Northern Range is marked by a major 1006 lithologic boundary along the previously mapped Chupara Fault (Kugler, 1961; De Verteuil et al., 2005). 1007 1008 The temperatures shown are calculated using the Aoya et al. (2010) and Lahfid et al. (2010) calibrations. b) Temperature $(\pm 1 \text{ s.e.})$ for samples along the north coast of the Northern Range calculated using a 1009 variety of RSCM calibrations. Lower temperature samples from the southwestern Chancellor Schist are 1010 excluded as they are separated from the higher temperature samples by the E-W trending Arima Fault. 1011 Average temperatures (1σ) of the eastern and western blocks are displayed as the blue-shaded regions. 1012

1013

Figure 8: Cooling history of the a) eastern and b) western Northern Range modified from the QTQt 1014 bedrock cooling models of Arkle et al. (2021). Timing of peak metamorphism is estimated by 40 Ar/ 39 Ar 1015 ages through the Northern Range (Speed et al., 1997, Weber & Arkle, 2015). In the east, the cooling 1016 path following peak metamorphic temperature, and possibly its timing, remains largely unconstrained 1017 1018 due to the disparity between un-reset ZFT ages and high RSCM temperatures, potentially indicating a short-lived thermal event. Dark and light grey lines are the expected cooling histories of the high and 1019 low elevation samples, respectively, with the shaded regions representing a 95% confidence interval 1020 (Arkle et al., 2021). 1021

1022

Figure 9: Cartoon showing tectonic evolution of the Northern Range and Araya-Paria, Venezuela,
metamorphic hinterland, modified from Arkle et al. (2021). a) Following Jurassic-Cretaceous rifting, the
area was dominated by passive margin deposition of sediment along continental South America. b)
Oblique plate collision led to peak metamorphism and thrust faulting in the Northern Range in the late
Oligocene. This time marks the inception of foreland and hinterland structures and of hinterland

- metamorphism. c) A transition to strike-slip plate motion between the Caribbean and South American
 plates produced structures such as the Gulf of Paria pull-apart basin. Eastward propagation of the STEP
 edge induced greater exhumation of the western Northern Range upon its arrival in Trinidad, which was
 accommodated by the Chupara Fault. d) Continued STEP propagation along the plate boundary led to an
 inversion in Northern Range exhumation and late Pliocene to recent surface uplift, with subsidence
 currently dominant in the west as the east experiences surface uplift (e.g., Arkle et al. 2017, 2021). NR –
 Northern Range; SdI Serranía del Interior; MB Maturin Basin; CR Central Range; SR Southern
- 1035 Range; CF Chupara Fault; NCFZ Northern Coastal fault zone; EPFZ El Pilar Fault zone; CB –
- 1036 Columbus Basin.
- 1037
- 1038 Figure S1: Plots of nominal temperatures calculated using 3- (Aoya et al., 2010; square symbols) and 5-
- band (Lahfid et al., 2010; plus signs) calibrations against the centers of fitted G bands. The G band of
- fully ordered graphite (1582 cm^{-1} ; Wang et al., 1990) is labeled by dashed lines for reference. The
- analyses at UNITO and ROM are denoted by black and blue colors, respectively.
- 1042

























Figure S1