1	Combining paleomagnetic and Re–Os isotope data to date hydrocarbon generation								
2	and accumulation processes								
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19	Key Points:								
20 21 22	• Palaeomagnetic and Re–Os isotope data were collected for a hydrocarbon carbonate reservoir to determine the hydrocarbon evolution processes.								
23 24 25	• Oil accumulations are found to have remagnetized the reservoir carbonates during the Late Triassic and Cretaceous.								
26 27 28	 Timing of oil generation is constrained by Re–Os dates of bitumen and oil hosted in carbonates at ~264 and ~94 Ma, respectively. 								
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33 Abstract

34 Unravelling the complex relationship between orogenesis and hydrocarbon formation and accumulation

35 is challenging and is often hampered by physical and chemical overprints of younger events. The

36 Permian reservoir in the Longmen Shan orogen, South China, is such an example, and its evolution has been hotly debated. In this study, we use a new combination of paleomagnetic dating analysis and Re-37 38 Os isotope dating to try to resolve this. Paleomagnetic dating of the hydrocarbon-host carbonate 39 indicates two remagnetization events during: (1) the Late Triassic, and (2) the Middle Jurassic-40 Cretaceous. These two remagnetization events are shown to represent two distinct stages of hydrocarbon accumulation. The paleomagnetic estimates are supported by Re-Os dating of bitumen 41 42 (~264 Ma) and oil (~94 Ma). The two different Re-Os ages are associated with two periods of oil 43 generation. We interpret these data in terms of known geological processes: (1) the ~260 Ma Dongwu 44 large igneous province caused oil generation, and the Indosinian tectonic event caused the migration 45 and accumulation; and (2) the Late Cretaceous Yanshan orogenic events promoted another generation 46 and entrapment of oil in the same reservoir. This combined approach reliably tracks the sequence of oil 47 generation and accumulation, even when the source rock is uncertain, and multi-phase accumulation 48 and complex tectonism has occurred. Given that paleomagnetic and Re-Os dating are independent 49 methods which can constrain multiple geological processes, when used together they have the potential 50 to be universally applied.

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52 Plain Language Summary.

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54 Key to understanding complex geological processes is the dates and sequence of each event. The 55 timing of hydrocarbon formation and accumulation is one such complex geological process that can be difficult to unravel, but critical to evaluate the complex orogenesis and hydrocarbon explorations. In 56 this paper, we combine for the first time two independent dating methods to study hydrocarbon 57 58 reservoirs of Longmen Shan orogen: (1) paleomagnetic and (2) rhenium-osmium isotope dating. The 59 two methods identified two periods of hydrocarbon formation, followed by two extended periods of hydrocarbon migration. This combined method is particularly powerful as it is independent of the 60 61 hydrocarbon source rock and complex geological settings. Moreover, the two methods can provide additional tests for each dating technique. The new combined methods can, therefore, be applied in 62 63 complex hydrocarbon-bearing regions worldwide.

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73 **1 Introduction**

Determining the spatial and temporal evolution of hydrocarbon reservoir systems helps us to improve yield from mature reservoir systems, thus reducing the need for further exploration as the world moves towards a carbon-free future. The evolution of such hydrocarbon systems can be problematic due to a number of processes, which can contribute to, for example, the maturation history of the source rocks, oil migration and accumulation patterns, hydrocarbon cracking or gas generation in reservoir rocks, and the destruction of hydrocarbon reservoir systems (e.g., Zhang et al., 2018, 2019).

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81 Key to understanding hydrocarbon reservoir evolution is quantifying the timing of formation of the 82 hydrocarbon and reservoir itself (Bhullar et al., 1999). There is no single method that consistently vields correct ages for hydrocarbon and reservoir formation. We propose combining two different 83 84 complementary methods for determining hydrocarbon evolution ages: (1) paleomagnetic dating 85 methods, and (2) Re-Os geochronology. Paleomagnetic dating has previously been carried out on 86 hydrocarbon-bearing rocks to provide time ranges of hydrocarbon generation, accumulation, and 87 destruction (Elmore et al., 1987; Elmore & Leach, 1990; Zhang et al., 2016, 2018, 2019). This method 88 requires isolation of the characteristic remanent magnetization (ChRM), assuming hydrocarbon 89 activities are related to remagnetization, and then comparison with the apparent polar wander paths 90 (APWP) of the region. Given the availability of quantitative relationships between magnetic and 91 hydrocarbon parameters, paleomagnetic ages can often be directly linked to hydrocarbon evolution 92 processes (e.g., Manning & Elmore, 2015; Zhang et al., 2016). However, the effectiveness of this method is limited by the accuracy of published APWP paths. Rhenium-osmium (Re-Os) 93 94 geochronology can be applied directly to crude oil and bitumen in reservoir rocks to determine absolute 95 ages (Georgiev et al., 2016; Selby et al., 2005). Interpreting these ages in the context of geological 96 processes is often difficult, however, as the hydrocarbon undergoes continuous modifications, which 97 could modify the Re–Os systematics throughout the petroleum history (Ge et al., 2016; Li et al., 2017; 98 Lillis & Selby, 2013). By combining these two entirely independent methods we aim to compensate for 99 each methods' limitations, allowing for temporal variations in hydrocarbon evolution to be more 100 accurately dated.

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102 To determine the effectiveness of these combined approaches, we used paleomagnetic and Re-Os 103 dating methods to study the Longmen Shan foreland thrust belt in South China (Figure 1), which 104 contains a complex hydrocarbon system in its northern part (Jia et al., 2006). The generation and 105 migration history of the hydrocarbons is uncertain. They may be the product of several accumulation 106 processes, and have been affected by multiple tectonic events since the Ediacaran, including the 107 Dongwu large igneous province and Caledonian, Indosinian, Yanshan and Himalayan orogenies (Figure 1d; Jia et al., 2006). In addition to paleomagnetic and Re–Os dating, we also measured the total 108 organic carbon (TOC) content, bitumen reflectance and ⁸⁷Sr/⁸⁶Sr isotope ratios to better characterize the 109 relationship between the remagnetization and hydrocarbon activities. 110

111 2 Geological Setting

The Longmen Shan foreland thrust belt is on the western boundary of the Sichuan Basin close to the 112 Tibetan Plateau. It is marked by a NE striking thrust belt with fault-related folds and the western 113 114 Sichuan foreland basin (Burchfiel et al., 1995; Jia et al., 2006; Figure 1a-c). Multiple tectonic events have happened in this area from the Permian to present, including the Dongwu large igneous province, 115 and the Indosinian, Yanshan, and Himalayan orogenies (Figure 1d). The ~260 Ma Dongwu large 116 igneous province relates to the mantle plume which produced the extensive Emeishan flood basalts 117 118 around the Sichuan Basin, and the unconformities in the Middle Permian strata (He et al., 2007; 119 Shellnutt, 2014). Subsequently, due to the closure of the Paleotethys between the South China, North China, and Qiangtang continental blocks, the Late Triassic Indosinian orogeny initiated deformation of 120 the Longmen Shan belt (Jia et al., 2006; Figure 1b). Meanwhile, Late Triassic Sichuan foreland basin 121 122 formed in the eastern part of Longmen Shan belt because of tectonic loading (Jia et al., 2006; Zhang et 123 al., 2015a; Figure 1c). The subsequent Yanshan orogeny, which occurred during Jurassic-Cretaceous in 124 this region, is the result of the East Asian and Siberia continent-continent collision and subduction of 125 paleo-Pacific plate (Dong et al., 2018). The Yanshan orogeny was tectonically relatively quiet, 126 generally lacking intense deformation. However, some unconformities, metamorphism and igneous 127 intrusions indicate that thrusting occurred; there was slow uplift of the Longmen Shan thrust belt and the continuous subsidence of the adjacent foreland basin (Li et al., 2012). The Cenozoic Himalayan 128 129 orogeny resulting from the India-Asia collision is the most recent event recorded in this region (Yan et 130 al., 2011, 2018). During this event, the present Longmen Shan belt formed through rapid uplift, 131 exhumation and deformation (Li et al., 2014; Wang et al., 2012).

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133 The Permian marine carbonate rocks in the Sichuan Basin are one of the most important reservoir rocks 134 in South China as they host the largest gas field of China — the Puguang gas field in the eastern 135 Sichuan Basin (Figure 1b). These reservoir rocks are well exposed in the northern portion of the 136 Longmen Shan belt (Figure 1), and comprise dolostone and bioclastic limestone of the Qixia Formation, and limestone of the Maokou Formation (Figure 1d). However, the superimposed tectonism mentioned 137 above, results in a complex hydrocarbon system, whose formation is a matter of debate. For example, 138 the hydrocarbon source rock has been proposed to be: (1) the black shales of the lower Cambrian strata 139 140 (Tan et al., 2022), (2) the Permian rocks in the region (Gao et al., 2020), (3) Silurian source rocks in 141 other regions (Xie et al., 2020), or (4) a mixture of these (Hu et al., 2021). Additionally, a wide range of hydrocarbon generation and accumulation dates have been proposed primarily from basin modeling, 142 with no consensus, for example, the Permian (Qiu et al., 2021), Triassic-Jurassic (Li et al., 2022), the 143 144 Cretaceous (Luo et al., 2020) and the Paleogene (Lu et al., 2017).

145 **3 Samples and Methods**

146 **3.1 Paleomagnetism**

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To characterize the remagnetization of the Permian reservoir, 182 hydrocarbon-bearing carbonate samples were collected from 23 sites distributed along both limbs of three folds in the thrust belt, i.e., the Zhuyuan, Changjianggou, and Chejiaba folds (Figure 1). Samples were either demagnetized thermally in an ASC TD-48 thermal demagnetizing oven at steps of 20-50°C to a maximum temperature of 570°C, or demagnetized in an alternating field (AF) at steps of 3-10 mT to a maximum of 100 mT. Magnetic measurements were conducted using a 2G-755 cryogenic rock magnetometer in the magnetic shielded room of Nanjing University. Orthogonal-projection plots were used to identify ChRM directions using a principal-component analysis of Kirschvink (1980) and software of Enkin (1994). For constraining the ages of the ChRMs with respect to folding, the fold test and progressivetilt tests were applied (Enkin, 2003; Tauxe & Watson, 1994; Tauxe et al., 2016).

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159 **3.2 Rock magnetic analysis**

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For estimating the magnetic mineralogy and the magnetic-minerals' grain-size distribution, isothermal remanent magnetization (IRM) acquisition curves were measured on 16 representative specimens at the paleomagnetic laboratory of Nanjing University. The IRM acquisition curves were obtained using an impulse magnetizer (ASC IM–10–30) and a spinner magnetometer (AGICO JR– 6A). The unmixing methods were used to analyze the results (Kruiver et al., 2001).

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167 To better quantify the mineralogy, a 'Lowrie test' was conducted (Lowrie, 1990). The specimens 168 were magnetized firstly along the z-axes using a field of 2.4 T, and then along y-axes with a field of 169 0.4 T and ultimately along x- axes using a field of 0.12 T. The samples were then heated to 680°C 170 during stepwise thermal demagnetization.

172 **3.3 Re–Os isotopes**

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174 Re-Os analysis was conducted to determine the ages of hydrocarbon formation. We undertook Re-Os 175 analysis on four oil and eleven bitumen samples from reservoir carbonate rocks where paleomagnetic 176 measurements were done, i.e., oil from the Zhuyuan fold, and bitumen from the Changjianggou and 177 Chejiaba folds (Figure 1). At the Durham Geochemistry Centre laboratory, ~100 mg of oil and ~150 178 mg of bitumen were dissolved in Carius tubes using 6 ml HNO₃ and 3 ml HCl for 24 hours at 220°C. and then equilibrated by the given amount of ¹⁸⁵Re and ¹⁹⁰Os tracer solution. Chloroform and micro-179 distillation were used to extract and purify Os from the acid solution. Subsequently, the NaOH-acetone 180 181 extraction and anion exchange chromatography were used to isolate the remaining Re bearing solution. 182 The Ni and Pt filaments were applied to load the isolated Re and Os fractions, and the isotope ratios were measured via a Thermo Scientific TRITON-Electron mass spectrometer. Finally, Re-Os data 183 were regressed via a toolkit (Isoplot V. 4.15) of Ludwig (2008) and a ¹⁸⁷Re decay constant (1.666×10⁻¹¹ 184 a^{-1}) of Smoliar et al. (1996). 185

187 **3.4 Scanning electron microscopy (SEM)**

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For further identifying the magnetic remanence carriers, scanning electron microscopy (SEM) was used to image typical polished sections. This was done using a field–emission–gun scanning electron microscope (Supra-55 Sapphire) equipped with an energy dispersive spectrometer (Oxford Aztec X-Max 150) at Nanjing University. Backscatter-electron images were used to easily identify the iron oxides or sulfides, and energy-dispersive X-ray spectroscopy (EDS) to describe the elemental contributions.

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196 **3.5 The Analysis of Total Organic Content, Bitumen Reflectance in oil and Strontium Isotopes**

To estimate the amount of hydrocarbon present in the samples, total organic content (TOC) was determined on 20 representative carbonate samples on which ChRMs were also determined. The bitumen reflectance (*Rob*) of five bitumen samples was measured to quantify maturity; this was accomplished at Nanjing University using an incident light microscope (Zeiss Axiokop 40 Pol) with a 50×0.85 oil immersion objective and at a wavelength of 546 nm. The *Rob* values were converted to the vitrinite reflectance (*Ro*) by using an equation $Ro = 0.618 \times Rob + 0.4$ of Jacob (1985).

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To characterize the fluids that potentially caused the remagnetization, we measured strontium isotope ratios (87 Sr/ 86 Sr) of 14 representative hydrocarbon-bearing carbonate samples on a TRITON mass spectrometer at Nanjing University. The values were normalized relative to SRM 987 = 0.710250 (± 13) (SRM = standard reference material). In order to calculate Permian 87 Sr/ 86 Sr ratios from present-day values, the Sr concentration of the samples was measured using an inductively coupled-plasma mass spectrometer (Aurora M90).

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212 **4 Results**

213 4.1 Paleomagnetic analysis

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215 From thermal and AF demagnetization data, most samples yielded reliable remanence directions 216 (Figure 2). A low temperature component was isolated $< 250^{\circ}$ C, which was similarly isolated for 217 alternating fields <15 mT (Figures 2a and 2b). The site-mean direction of this component (Declination = 356°, Inclination = 51°, number of sites = 27, α_{95} = 3°) is similar to the present-day field. Higher-218 219 temperature components with direction differences were isolated between ~280°C and 370°C-480°C; 220 there were corresponding components identified using AF demagnetization, i.e., AF = 15-50 mT. 221 These components were the characteristic magnetizations, the ChRMs (Table 1). Two ChRMs were 222 identified: (1) ChRM-1 was found in 13 sites, and is characterized by mean values of declination (Dg) = 41°, inclination (Ig) = 47° (α_{95} = 4°) in geographic coordinates, and a declination (Ds) = 43°, 223 224 inclination (Is) = 48° (α_{95} = 20°) in stratigraphic coordinates (Figures 2c and 2e); (2) ChRM-2 was 225 found in 10 sites, with a mean $Dg = 18^\circ$, $Ig = 48^\circ$ ($\alpha_{95} = 4^\circ$) in geographic coordinates, and $Ds = 44^\circ$, Is226 = 49° (α_{95} = 34°) in stratigraphic coordinates (Figures 2d and 2f). Most ChRM-1 directions occur in 227 samples from the Chejiaba and Changjiagou folds, while most ChRM-2 occur in samples from the 228 Zhuyuan fold. To constrain the ages of the ChRMs with respect to folding, a fold test and progressive 229 tilt test were conducted. The results of the fold test are negative for the ChRMs (Figures 2c-f), suggesting that these carbonate rocks were remagnetized after the formation of the folds during the 230 231 Triassic (Enkin, 2003; Tauxe et al., 2016; Tauxe & Watson, 1994). The progressive tilt test exhibits 232 similar results, with maximum K values at 4.4% and 3.9% unfolding (Figure 3). The fold test of Tauxe 233 and Watson (1994) show maximum K values at $-3\% \sim 8\%$ unfolding for ChRM-1 and maximum K 234 values at -1%~7% unfolding for ChRM-2 (Figure 4).

- 235236 4.2 Rock magnetic analysis
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Representative samples from different regions and lithology were chosen for IRM analysis, and typical curves are shown in Figure 5. Most samples show a typical curve of low to medium coercivity magnetic minerals, as they reach ~80% of saturation IRM before 0.2 T (Figures 5a and 5b). In contrast,

241 two samples (CJG04 and CJG06; Figures 5b) did not reach saturation in a field of 1.0 T and 2.4 T, 242 which is a characteristic of hard coercivity remanence carriers (e.g., Yang et al., 2004). To analyze the IRM acquisition curves, the unmixing approach of Kruiver et al. (2001) was applied (Figures 5c-h; 243 244 Table S1). In this approach, the IRM acquisition curves are manually unmixed into components 245 assuming lognormal distributions; the components are characterized by their mean coercivity $(B_{1/2})$, 246 saturation IRM and half-width of the distribution (DP). For example, for sample CJG06 two 247 components were identified. There is a 'hard' magnetic component with $B_{1/2} \sim 1737$ mT and DP ~ 0.2 , which potentially corresponds to hematite, and a 'soft' component (18%) with $B_{1/2} \sim 56$ mT and DP ~ 248 0.36. Generally, for most samples two components were identified (e.g., CJB04 and CJB08 in Figures 249 5e and 5g): (1) a 'soft component' making up 65%–99% of IRM contributions with $B_{1/2} \sim 40$ to 56 mT, 250 and (2) a 'hard component' with $B_{1/2} \sim 501$ to 2512 mT. The 'soft' component is indicative of a 251 252 magnetite-like phase, and the 'hard' a hematite-like phase.

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254 The samples were subjected to a 'Lowrie' test (Lowrie, 1990; Figure 6) to try to identify the magnetic 255 mineralogy. Most samples were dominated by the soft fraction, demagnetizing between 400–570°C, 256 and likely indicating magnetite. There was also a medium and hard fraction. For the samples CJB04 257 and CJB07, the unblocking temperatures of the hard fractions were ~680°C, indicating the presence of hematite. For the samples CJB04, CJB07 and ZY02, the soft or medium fractions at ~325°C suggest an 258 259 iron-sulphide ferromagnetic (s.l.) phase likely pyrrhotite or greigite. For samples CJB08 and ZY02, the 260 final demagnetization temperature of both medium and hard fractions was at ~350°C, indicating an 261 absence of hematite in these samples. 262

- 263 **4.3 Re–Os isotopes**
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The Re–Os isotopic analysis of oil and bitumen produced two sets of date results. The four oil samples 265 contain between 8.4-46.8 ppb Re and 198.0-600.6 ppt Os, with ¹⁸⁷Re/¹⁸⁸Os and ¹⁸⁷Os/¹⁸⁸Os ratios of 266 194.8–562.7 and 1.29–1.87, respectively (Table 2). The Re–Os data of the oil samples produce a Model 267 3 date of 94 ± 10 Ma, with an initial 187 Os/ 188 Os value of 0.994 ± 0.061 (MSWD = 3.7; Figure 7a). The 268 eleven bitumen samples contain 7.7-80.7 ppb Re and 97.3-669.0 ppt Os, with ¹⁸⁷Re/¹⁸⁸Os and 269 ¹⁸⁷Os/¹⁸⁸Os ratios of 102.5–2903.6 and 2.3–15, respectively. The bitumen samples produce a Re–Os 270 date of 268 ± 17 Ma (Model 3), with an initial ¹⁸⁷Os/¹⁸⁸Os value of 1.60 ± 0.35 (MSWD = 541; Figure 271 7b). The bitumen Re-Os date estimate does, however, have a large MSWD and a Model 3 fit, 272 273 indicating that significant geological scatter exists in addition to analytical uncertainties (Ludwig, 2008). The bitumen originating from several different source rocks is suggested to be the primary cause 274 of the scatter in the dataset, which resulted in large variation of initial ¹⁸⁷Os/¹⁸⁸Os ratios (Selby et al 275 2005). The initial ¹⁸⁷Os/¹⁸⁸Os ratios of 6 out of the 11 bitumen samples at 268 Ma are similar, ranging 276 from 1.2 to 1.6 (samples Bitumen-1, 2, 4, 6, 7 and 9), indicative of a similar origin. This subset of 277 278 samples produces a Re–Os date of 264 ± 16 Ma, with a lower degree of scatter (MSWD = 42; Figure 279 7b).

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281 4.4 SEM analysis

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SEM imaging found that the matrix for the reservoir rock is typically constituted by carbonate, fractures and pores (Figure 8). In most hydrocarbon-bearing samples, bitumen can be observed along the fractures or in the pores (Figures 8a–c); EDS analysis of the bitumen identified sulfur and carbon (Figure 8g). Fine-grained iron oxides (generally $<10 \ \mu m$ in diameter) occur as disseminated grains and framboidal clusters along bitumen-filled fractures and pores (Figure 8). Together with the rock magnetic results, most of these iron oxides are likely authigenic magnetite, although a few hematite grains may occur (Elmore et al., 1987, 2012). Iron sulfides can also be observed presented in framboidal forms in the matrix, some of which are not in the fractures. Together with the EDS analysis, most of the iron sulfides should be pyrite (Figures 8a and 8h), ferrimagnetic iron-sulfides may also be present (Figures 8f and 8j), e.g., greigite.

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294 **4.5** The analysis of Total Organic Content, Bitumen Reflectance in oil and Strontium Isotopes

A group of 20 hydrocarbon-bearing samples were selected for the TOC measurement. The values range from 0.01 to 0.78 wt. % (Table S2), and is positively correlated with the natural remanent magnetization (NRM) with a Pearson's correlation coefficient R = 0.78 (Figure 9). This phenomenon has been reported previously for hydrocarbon-rich rocks (Emmerton et al., 2012; 2013)

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The vitrinite reflectance (Ro) was converted from bitumen reflectance, which was measured on five representative bitumen samples. The mean Ro values range from 0.9% to 1.2%, maximum Ro values range from 1.0% to 1.4%, and minimum Ro values from 0.7% to 0.9% (Table S3). Thirteen carbonate samples yielded ⁸⁷Sr/⁸⁶Sr ratios in a narrow range of 0.70704–0.70731, and the sample of ZY4-10 yielded a higher ratio of 0.70794 (Table S4). All of these values are inside the isotopic scope of contemporaneous Permian seawater (0.7070–0.7080) (McArthur et al., 2012; Figure 10).

307 5 Discussion

308 Based on the paleomagnetic demagnetization data, two ChRM directions were identified in the 309 hydrocarbon-bearing carbonate samples from the northern portion of Longmen Shan belt. Fold tests 310 suggest that both ChRMs were acquired post-folding. The ChRM directions are thought not to be the 311 result of regional block rotations, due to the similarity between the primary geomagnetic result of 312 Permian-lower Triassic strata in the studied region and those in the stable areas in South China (Heller 313 et al 1988; Li & Wang, 1989; Steiner et al., 1989). Disregarding vertical axis rotations, a comparison of 314 the paleopole determined from the ChRMs with the APWP of South China (Figure 2g) indicates that 315 the two mean ChRM directions were acquired during two separate time periods, the Late Triassic and 316 Middle Jurassic-Cretaceous. The ages of both ChRMs post-date the deposition of the hydrocarbonbearing carbonate, which, together with the negative fold test results, indicates that both ChRMs are 317 secondary remanent magnetizations. Based on the rock magnetism, the ChRMs are mainly carried by 318 319 magnetite, which can be observed as authigenic magnetite in the back-scatter images. The evidence that 320 the ChRMs are chemical remagnetizations is twofold: (1) the low vitrinite reflectance values of bitumen, i.e., 0.9–1.2%, indicate temperatures < 200°C, and (2) authigenic magnetite – the main carrier 321 322 of the ChRMs – was widely observed within bitumen-filled fractures (Figure 8).

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5.1 The origin of the remagnetization events in the reservoir carbonate

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This remagnetization was most likely due to the migration and accumulation of hydrocarbon fluids within the Permian carbonates (Machel, 1995; Zhang et al., 2018). This argument is supported by three lines of evidence: (1) in the oil- and bitumen-rich carbonate rocks, authigenic magnetite was commonly 329 observed co-existing with hydrocarbons (Figure 8), (2) the Permian carbonate contains a high amount 330 of oil and bitumen, with NRM intensities (a reflection of magnetite content) correlated with TOC (a 331 reflection of the hydrocarbon content; Figure 9), and (3) the Sr isotope composition of the carbonate 332 rocks indicate that they were not significantly altered by chemically evolved orogenic fluids (Figure 333 10). These three characteristics have previously been used to associate the acquisition of chemical 334 remagnetization to hydrocarbon accumulation (Elmore et al., 1987; Elmore & Leach, 1990; Zhang et 335 al., 2018). The same association can be employed here; we link the two remagnetization events to two 336 stages of hydrocarbon migration and accumulation, one during the Late Triassic and the other during 337 the Middle Jurassic-Cretaceous.

338 The chemical processes leading to magnetic mineral formation in the presence of hydrocarbons is complex, and depends on the complex interplay between the host reservoir rocks, sulfur content of the 339 340 hydrocarbons, origin of the hydrocarbons, the redox conditions and temperature/depth of remagnetization (Machel, 1995; Badejo et al., 2021: Abdulkarim et al., 2022; Perkins, 2022). Generally, 341 hydrocarbons produce reductive environments leading to the formation of iron sulphides (Machel, 1995; 342 Zhang et al., 2018), however, in very low-sulfur hydrocarbon environments, magnetite formation has 343 344 been widely observed and reported (e.g. Perkins, 2022). Perkins (2022) suggest that the magnetite is 345 formed in relatively small quantities during the dehydroxylation of goethite to hematite, however, 346 given magnetite's relatively strong magnetic properties, it dominates the NRM.

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348 5.2 Linking Re–Os isotope ages to hydrocarbon evolution

350 Rhenium–Os data from crude oil in the remagnetized carbonates yielded an absolute age of 93.8 ± 9.8 351 Ma (Figure 7a), which indicates that hydrocarbon evolution reset the Re-Os system. Two potential 352 mechanisms which are thought to reset the Re-Os geochronometer are oil generation (e.g., Cumming et 353 al., 2014; Georgiev et al., 2016; Selby & Creaser, 2005) and hydrothermal alteration (e.g., Lillis & Selby, 2013). Given that the ⁸⁷Sr/⁸⁶Sr isotope compositions of the Permian carbonate rocks are within 354 355 the isotopic range of Permian seawater, significant hydrothermal alteration of crude oil seems to be less 356 likely. Recent geochemical analysis of the same reservoir, also found no evidence for hydrothermal 357 alteration (Xiao et al., 2021). Oil generation is therefore suggested as the most likely origin of crude oil 358 Re–Os age.

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360 The bitumen samples show a Re–Os age of 264 ± 16 Ma (Figure 7b). As bitumen is a secondary 361 product that evolves from liquid oil following oil generation and migration, various formation mechanisms are possible. These mechanisms are generally divided into two categories: 1) thermal 362 cracking resulting in pyrobitumen marked by higher vitrinite reflectance values, and 2) mechanisms 363 unconnected to thermal cracking such as water washing and biodegradation (Jacob 1985; Larter et al., 364 2006; Li et al., 2020; Mastalerz et al., 2018; Shalaby et al., 2012). Neither water washing nor 365 biodegradation was considered to notably influence Re-Os isotope systematics (Finlay et al., 2011; 366 Lillis & Selby, 2013; Selby et al., 2005). Additionally, post-accumulation disturbances that chemically 367 368 react with hydrothermal fluids can alter Re–Os systematics (Lillis & Selby, 2013); however, using the 369 same reasoning given above for oil, we dismiss hydrothermal alteration as a likely origin of bitumen 370 Re-Os age. Therefore, bitumen Re-Os ages are primarily associated with oil generation and thermal 371 cracking (Ge et al., 2016; Selby et al. 2005). Of the two remaining possible mechanisms, we suggest that the oil generation is the most likely, because the vitrinite reflectance data for the bitumen samples are generally lower than those for gas generation and oil cracking (Ro > 1.3; Mastalerz et al., 2018).

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375 **5.3** Combined remagnetization and Re–Os isotopes age analysis

377 It is likely that the Re–Os ages for the hydrocarbon samples and the remagnetization data for the 378 hydrocarbon-bearing carbonate yield ages are related to the same process of hydrocarbon evolution. In 379 this natural process, the hydrocarbon generation should occur prior to or coeval with hydrocarbon accumulation, and the oil cracking and hydrothermal alteration should occur after oil accumulation. 380 381 Therefore, we determined that the age of earlier oil generation is ~264 Ma based on the Re-Os age of 382 bitumen, which agrees with the oil accumulation age during the Late Triassic based on the 383 remagnetization ChRM-1 (Figure 11). Similarly, the second oil-generation age based on the Re-Os data 384 for crude oil is ~94 Ma, which agrees with the broad age range for ChRM-2, i.e., covering the Middle 385 Jurassic-Cretaceous. This combined study can now limit the age range into the Late Cretaceous. 386 ChRM-2 is broad because of overlapping pole positions for the APWP of South China during Middle 387 Jurassic–Cretaceous (Figure 2g).

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389 By using the combined method, we can track two periods of hydrocarbon evolution, even without prior 390 knowledge of the source rocks and complexity of the system. In the first stage, the oil generated at the 391 age of ~264 Ma and possibly migrated into an initial reservoir. Until the Late Triassic, the oil 392 subsequently migrated into the Permian reservoir rocks studied here. In the second stage, another generation of oil occurred at the age of ~94 Ma, which migrated and then was trapped in the same 393 394 Permian reservoir. These new ages are big improvements on previous age estimates for hydrocarbon 395 evolution in the Longmen Shan belt, based mainly on basin models, which themselves rely on often 396 poorly constrained parameters such paleo-heat flow, strata thickness etc. (Li et al., 2022; Lu et al., 2017; 397 Luo et al., 2020; Oiu et al., 2021). These poorly constrained models yield a wide range of hydrocarbon 398 evolution ages from the Permian to Paleogene, although there is a consensus on three characteristics: (1) 399 multiple hydrocarbon activities have occurred; (2) a secondary migration for the earlier hydrocarbon 400 activity happened; (3) faults are the primary migration pathways.

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402 **5.4 Hydrocarbon evolution and tectonic events in the studied regions**

404 Hydrocarbon generation and accumulation is a dynamic process relying on depth and temperature, and pathways and trapping, all of which can be related to tectonic events (Philippi, 1965). Here we link 405 406 hydrocarbon evolution to three phases of tectonism mainly based on temporal links and the results of 407 the fold test (Figures 3, 4 and 11). Firstly, our study shows hydrocarbons were initially generated 408 at~260 Ma, which is similar in age to the ~260 Ma Dongwu large igneous province which occurred 409 around the Sichuan Basin (Li et al., 2015; Shellnutt, 2014). It is very likely that the study region was significantly influenced by this thermal event, leading to the oil generation. This is supported by U-Pb 410 ages for nearby diabase dykes (~261 Ma; Shen et al., 2018). Secondly, based on the negative fold test 411 412 (Figures 3 and 4), we suggest that the Late Triassic Indosinian thrusting would have faulted and folded 413 the region to form the suitable migration paths and entrapment structures, e.g., the Changjianggou and 414 Chejiaba folds (Yan et al., 2011). These Indosinian event connected the initial reservoir through faults, 415 resulting in the hydrocarbon's secondary migration and accumulation in the studied Permian reservoir. Thirdly, continued thrusting during the Cretaceous Yanshan event led to subsidence of the adjacent foreland basin (Li et al., 2012), increasing burial depth and temperature promoting a second phase of oil generation at 94 ± 10 Ma. The oil was subsequently mobilized and trapped in the pre-existing folds formed by the Indosinian events, indicating that the Yanshan event may not significantly change the pre-existing folds, but have re-activated existing thrust faults to provide migration paths. The apatite fission track ages in the Longmen Shan belt also indicate that the Late Cretaceous was the most intense episode of the Yanshan orogeny (Li et al., 2012; Xu, et al., 2018).

423

In summary, although the northern portion of Longmen Shan orogen records extensive superimposed tectonism, it is during the Indosinian tectonic event that the main geological structures that allowed for migration and entrapment of hydrocarbon, formed. The Dongwu magmatism and Yanshan tectonism provided the heat for hydrocarbon maturation, and the latter may also have re-actived migration paths. It is suggested that the Cenozoic Himalayan, which is thought to be significant in the formation of the Longmen Shan belt (Li et al., 2014; Wang et al., 2013), did not significantly affect the hydrocarbons in the region.

431

432 **6.** Conclusion

433

434 A combination of paleomagnetic and Re-Os isotope data acquisition and analysis has been conducted 435 on a complex carbonate reservoir in the northern portion of the Longmen Shan belt. With the new data we determined the sequence of hydrocarbon evolution, from generation to migration to accumulation, 436 and we relate these processes to regional orogenesis. We show that there are two periods of 437 438 hydrocarbon generation at ~264 Ma and ~94 Ma, the former associated with the ~260 Ma Dongwu 439 large igneous province, and the latter with the Yanshan orogenic events; there are also two periods of 440 hydrocarbon accumulation during the Late Triassic and Cretaceous, the former associated with the Late 441 Triassic Indosinian orogeny. Such geochronological information can be used to calibrate uncertain 442 basin modelling parameters, and reduce uncertainty associated with exploration in the future.

443

444 Due to other possible mechanisms of remagnetization and resetting of Re–Os isotope systems, 445 including hydrocarbon generation, cracking and hydrothermal alteration, combining these two methods 446 has the potential to constrain a range of critical hydrocarbon processes, providing more credible 447 information than a single method alone. The combined methods employed here should be applicable 448 globally, when: 1) complex hydrocarbon evolution process need to be characterized, especially without 449 a firm understanding of geological settings, and 2) the interpretation of each single method needs to be 450 strengthened.

451

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453

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458

459 Data Availability Statement

460 The data for this work could be downloaded on the website of 461 https://doi.org/10.6084/m9.figshare.21905895.

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 - 689

690 **Table Captions**

691

692 **Table 1.** Summary of site-mean ChRM directions of Permian shale and carbonate rocks from the

693 northern portion of the Longmen Shan Belt. Strike/dip are the bedding as measured in the field (right

hand rule), N is the number of directions used to determine the ChRM, Dg and Ig are the geographic

695 declination and inclination, and *Ds* and *Is* the stratigraphic declination and inclination, *k* the precision

696 parameter and α_{95} the standard confidence error.

- **Table 2.** Rhenium–Osmium content and isotopic composition for oil and bitumen samples from
- 700 Permian reservoir rocks, which paleomagnetic measurements were done. ppb = part per billion, ppt =
- 701 part per trillion and rho = the associated error correlation.

704 Figure Captions

Figure 1. Simplified geological maps of: (a) China, (b) the Sichuan Basin and its surrounding blocks, PGF is the Puguang gas field. (c) The northern Longmen Shan belt, (d) a stratigraphic column of the western Sichuan Basin (modified from Jia et al., 2006). In (c) the distribution of Cambrian–Cretaceous units and faults are shown, in addition to the sampling locations for this study. Each sampling location symbol in the map contains 1–7 sampling sites, which are spaced tens of meters to several kilometers apart.

- 712 Figure 2. Paleomagnetic data: (a) progressive thermal demagnetization data of sample CJG5-5, which
- 713 is a typical ChRM-1-bearing sample; (b) progressive alternating demagnetization data of sample
- 714 CJB05-9-IS, which is a typical ChRM-2-bearing sample; (c) site-mean data in situ coordinates for
- 715 ChRM-1-bearing samples; (d) site-mean data in situ coordinates for ChRM-2-bearing samples; (e)
- 716 site-mean data in tilt-corrected coordinates for ChRM-1-bearing samples; (f) site-mean data in tilt-
- corrected coordinates for ChRM-2-bearing samples; (g) In the APWP of South China Block (Zhang et
- al., 2015b), virtual geomagnetic poles were plotted. In (a) and (b), the blue lines represent viscous
- remanent magnetization and the red (ChRM-1) and orange (ChRM-2) lines highlight the picked ChRM
- directions. In (c), (d) and (g), the red and orange stars denote the average directions of the ChRM-1 and
- 721 ChRM-2, respectively.
- 722

- 723 Figure 3. Results for the progressive tilt test and direction-correction test (Enkin, 2003) of ChRM1 (a-
- b) and ChRM2 (c–d). In (a) and (c), the maximum value of precision parameter (K) occurs at ~0%
- vuntil no set the set of the set
- 726 with black solid line, indicating a negative tilt test.

- Figure 4. Results of the fold test using the approach of Tauxe and Watson (1994) for: (a) ChRM-1
- samples and (b) ChRM-2 samples. The black line is the maximum eigenvalue as an unfolding function.
- 730 The red lines are the boot-strapping estimates used to estimate the green line, which is the cumulative
- 731 distribution function of the unfolding percentage. The blue lines are the 95% confidence boundaries for
- the green line.
- 733

- 734 **Figure 5.** (a–b) IRM acquisition curves of typical samples from the three folds and different lithologies
- as labeled in the legends; (c–h) typical IRM analysis charts through the approach of Kruiver et al.
- 736 (2001). As exhibited are linear acquisition plot, gradient acquisition plot and standardized acquisition
- plot for (c) CJG01, (d) CJG02, (e) CJB04, (f) CJB07, (g) CJB08 and (h) ZY02. The data were listed in
- the Table S1, which were available on the website of <u>https://doi.org/10.6084/m9.figshare.21905895</u>.

- 740 Figure 6. Triaxial IRM thermal demagnetization curves of representative samples from three folds and
- 741 different lithology: (a) CJG01, (b) CJG02, (c) CJB04, (d) CJB07, (e) CJB08 and (f) ZY02. Three
- perpendicular fields were applied before thermal demagnetization: 0.12 T, 0.4 T and 2.4 T. The
- coercivity value of soft fraction should be in the range of 0-0.12 T, the medium fraction is in the range
- of 0.12-0.4 T and the hard fraction is in the range of 0.4-2.4 T.

- Figure 7. ¹⁸⁷Re/¹⁸⁸Os versus ¹⁸⁷Os/¹⁸⁸Os binary diagrams for oil (a) and bitumen (b) from Permian
- 747 carbonate reservoir samples. Ellipses on data points represent 2σ absolute uncertainty. MSWD = mean
- squared weighted deviation. See Table 2 for the Re-Os data.

- 750 **Figure 8.** Backscatter electron images of representative Permian carbonate reservoir samples. Bitumen
- and iron oxide grains are distributed along fractures (a–c) and in pore spaces (d, e). The iron oxides
- often occur around the fractures, pores and bitumen. Typical EDS spectra for bitumen, magnetite and
- 753 iron sulfides are depicted in figures (g)–(j); the locations are shown in (a)–(f).

Figure 9. NRM versus TOC for carbonate reservoir samples. A linear regression trend-line is plotted.

- **Figure 10.** ⁸⁷Sr/⁸⁶Sr curves of Permian strata in this study and contemporaneous seawater. The orange
- 758 lines exhibit the Sr isotope values for our representative samples. The black and yellow lines show the
- 759 Sr isotope values of coeval seawater, which were modified from Wang et al. (2018) and McArthur et al.
- 760 (2012). The grey and blue fields exhibit the Sr error scopes.
- 761
- 762

- **Figure 11.** Relationship between hydrocarbon evolution and tectonic events, showing a comparison of
- the remagnetization time, Re–Os ages, U–Pb ages (Shen et al., 2018), ⁴⁰Ar–³⁹Ar (Yan et al., 2011) and
- 765 apatite fission track ages (Li et al., 2012).

Figure 1.



Figure 2.



Figure 3.



Figure 4.



Figure 5.



Figure 6.



Figure 7.



Figure 8.





(e) Iron oxides (i)





i µm

Signal A = AsB WD = 8.6 mm Supra 55





Figure 9.



TOC (%)

NRM (10⁻⁵ A/m)

1.0

Figure 10.

Series	Stage	Age (Ma)	0.7	7070	8 0.7	⁸⁷ Sr 074	7/ ⁸⁶ Sr 0.7078	0.7082
Lopingian	Wuchiapingian	255						
ian	Capitanian	260						
Guadalup	Wordian	265						ZY4-10
	Roadian	270						
Cisuralian	Kungurian	275 280						
	Artinskian	285						
	Sakmarian		•					
	sselian	295						







Figure 11.



Table 1. Summary of site-mean ChRM directions of Permian shale and carbonate rocks from the northern portion of the Longmen Shan Belt. Strike/dip are the bedding as measured in the field (right hand rule), N is the number of directions used to determine the ChRM, Dg and Ig are the geographic declination and inclination, and Ds and Is the stratigraphic declination and inclination, k the precision parameter and α_{95} the standard confidence error.

Site	Location	Lithology	Strike/dip	ChRM	N	Dg (°)	Ig (°)	Ds (°)	ls (°)	k	a95 (°)
Changjianggou Fold											
CJG01	32.321°N, 105.453°E	Limestone	33/33	ChRM-1	7	49	54	79	35	17	15
CJG02	32.324°N, 105.452°E	Limestone	32/40	ChRM-1	7	40	53	73	37	28	12
CJG03	32.297°N, 105.390°E	Limestone	215/36	ChRM-1	6	40	52	0	42	36	11
CJG04	32.288°N, 105.396°E	Limestone	215/36	ChRM-1	4	44	47	8	40	38	15
CJG05	32.290°N, 105.398°E	Limestone	215/42	ChRM-1	7	44	47	3	38	37	10
CJG06	32.293°N, 105.390°E	Limestone	229/82	ChRM-2	7	23	42	3	-13	48	9
Chejiaba Fold											
CJB01	32.534°N, 105.739°E	Limestone	71/66	ChRM-1	7	49	32	95	32	35	10
CJB02	32.534°N, 105.739°E	Limestone	71/66	ChRM-2	6	21	43	111	53	107	7
CJB03	32.534°N, 105.739°E	Limestone	77/57	ChRM-1	6	32	48	115	53	32	12
CJB04	32.534°N, 105.739°E	Limestone	77/57	ChRM-2	7	18	46	115	63	86	7
CJB05	32.534°N, 105.739°E	Dolomite	73/66	ChRM-2	11	16	52	129	52	57	6
CJB06	32.534°N, 105.739°E	Dolomite	73/66	ChRM-1	8	35	51	120	43	29	11
CJB07	32.526°N, 105.741°E	Limestone	82/48	ChRM-1	6	35	44	100	60	62	9
CJB08	32.520°N, 105.750°E	Limestone	215/36	ChRM-2	13	16	56	346	33	50	6
CJB09	32.511°N, 105.754°E	Limestone	235/34	ChRM-1	10	39	42	17	27	51	7
CJB10	32.511°N, 105.754°E	Dolomite	234/26	ChRM-1	11	38	55	9	40	98	5
			Zh	uyuan Fold							
ZY01	32.221°N, 105.292°E	Limestone	213/49	ChRM-2	11	20	53	344	25	109	4
ZY02	32.221°N, 105.292°E	Limestone	213/49	ChRM-1	8	33	48	353	30	137	5
ZY03	32.220°N, 105.292°E	Limestone	219/46	ChRM-2	8	18	55	346	23	83	6
ZY04	32.218°N, 105.285°E	Limestone	232/54	ChRM-1	9	53	36	23	21	39	8
ZY05	32.205°N, 105.299°E	Limestone	39/64	ChRM-2	7	20	39	71	31	37	10
ZY06	32.204°N, 105.312°E	Limestone	36/64	ChRM-2	8	11	46	75	36	127	5
ZY07	32.204°N, 105.312°E	Limestone	44/64	ChRM-2	8	14	47	85	39	88	6

Batch/Sample	Re (ppb)	±	Os (ppt)	±	¹⁸⁷ Re/ ¹⁸⁸ Os	±	¹⁸⁷ Os/ ¹⁸⁸ Os	±	rho
Oil1	13.6	0.04	241.5	1.6	319.3	2.6	1.507	0.015	0.704
Oil2	46.8	0.12	492.1	2.6	562.7	3.0	1.869	0.012	0.660
Oil3	21.1	0.06	600.6	3.0	194.8	1.2	1.293	0.009	0.650
Oil4	8.4	0.03	198.0	1.5	238.2	2.7	1.361	0.019	0.722
Bitumen-1	32.3	0.08	196.0	1.9	1752.5	15.1	9.356	0.086	0.861
Bitumen-2	15.2	0.04	97.3	1.4	1532.7	25.2	8.018	0.150	0.860
Bitumen-3	72.4	0.18	354.4	3.5	2903.6	21.0	15.082	0.121	0.794
Bitumen-4	22.1	0.06	144.1	1.6	1541.7	17.1	8.478	0.102	0.872
Bitumen-5	80.7	0.20	659.9	4.5	1000.4	4.8	5.468	0.031	0.616
Bitumen-6	13.6	0.04	443.5	2.8	190.4	1.2	2.322	0.018	0.650
Bitumen-7	12.2	0.03	423.1	2.7	179.1	1.1	2.371	0.019	0.654
Bitumen-8	15.6	0.04	524.7	3.4	189.8	1.2	2.630	0.020	0.650
Bitumen-9	15.6	0.04	459.7	2.9	213.6	1.3	2.460	0.019	0.657
Bitumen-10	18.3	0.05	669.0	4.3	173.9	1.0	2.593	0.020	0.647
Bitumen-11	7.7	0.02	476.5	4.1	102.5	1.0	2.579	0.032	0.676

Table 2. Rhenium–Osmium content and isotopic composition for oil and bitumen samples from Permian reservoir rocks, which paleomagnetic measurements were done. ppb = part per billion, ppt = part per trillion and rho = the associated error correlation.



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