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Phosphorus-limited conditions in the early Neoproterozoic ocean maintained low levels of atmospheric oxygen

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ABSTRACT: The redox chemistry of anoxic continental margin settings evolved from widespread sulphide-containing (euxinic) conditions to a global ferruginous (iron-containing) state in the early Neoproterozoic (1 to ~0.8 billion years ago, Ga). Ocean redox chemistry exerts a strong control on the biogeochemical cycling of phosphorus (P), a limiting nutrient, and hence on primary production, but the response of the P cycle to this major ocean redox transition has not been investigated. Here, we use a P speciation technique to investigate the phase partitioning of phosphorus in an open marine, early Neoproterozoic succession from the Huainan Basin, North China. We find that effective removal of bioavailable P in association with iron (Fe) minerals in a globally ferruginous ocean resulted in oligotrophic (nutrient limited) conditions, and hence a probable global decrease in primary production, organic carbon burial and, subsequently, oxygen production. Nevertheless, P availability and organic carbon burial were just sufficient to maintain an oxidising atmosphere. These data imply significant nutrient-driven variability in atmospheric oxygen levels through the Proterozoic, rather than the stable levels commonly invoked.

Phosphorus is generally considered the ultimate limiting nutrient on geological timescales[1], and is thus a key element in controlling primary productivity, organic C (C_{org}) burial, and consequently oxygen production. Atmospheric oxygen models suggest that after the Great Oxidation Event (GOE), pO_2 remained well below the present atmospheric level (PAL), with estimates ranging from <0.001 to ~0.4 PAL [2–4]. Furthermore, it is generally inferred that atmospheric oxygen may have remained at relatively constant levels after ~2.0 Ga, until the later Neoproterozoic (~0.8 to 0.542 Ga; refs 3,5,6). However, evidence for fluctuations in both the extent of ocean oxygenation[4,7] and the global-scale nature of ocean redox conditions[8,9] in the interim, could suggest variations in atmospheric oxygen concentrations.

The role of P bioavailability in controlling atmospheric oxygen between the GOE and the later Neoproterozoic is poorly constrained. Attempts to reconstruct dissolved P concentrations in the Precambrian ocean have relied on P contents of black shales and iron-rich chemical deposits[10–12]. In the latter case, the assumption is that P contents in iron formations provide a first order estimation of dissolved P in the water column, with only minimal remobilisation during diagenesis[10]. However, conflicting experimental determinations of P co-precipitation and adsorption coefficients have led to widely divergent reconstructions of Precambrian P concentrations[11,13,14].

In contrast to iron-rich chemical sediments, shales P content offers the significant advantage of a continuous record through the entire geologic timescale. This record has led to the suggestion that oceanic phosphate concentrations were extremely low until ~0.8 Ga[12], which might support inferences of extremely low atmospheric pO_2 (<0.001 PAL) until the Neoproterozoic rise in atmospheric oxygen[2]. However, bulk shale P contents are limited in that they do not specifically track bioavailable P. In addition, bulk shale P contents cannot provide detailed understanding of the extent of P recycling from the sediment back to the water column, which is highly dependent on the precise redox state of both the water column and sediment pore waters[15].

The flux of P to marine sediment commonly occurs *via* the transport of detrital apatite, organic matter and Fe minerals through the water column. During deposition under oxic conditions, up to 90% of C_{org} may be re-mineralised, releasing organic P back to the water column. However, under ferruginous conditions, bacterial P accumulation[16] and P uptake by iron minerals such as ferrihydrite[17] and green rust[18,19] in the water column may be particularly significant sinks for P. Upon settling, P may be released to pore waters and the water column during anaerobic diagenesis, *via* partial decomposition of organic matter and the reduction of Fe (oxyhydr)oxides[20–23]. This process may be compensated by re-adsorption onto Fe minerals at the sediment-water interface[24], enhancing sedimentary P fixation in association with crystalline Fe oxides[25] or Fe phosphates[19,26–28]. By contrast, phosphorus recycling back to the water column may be particularly intense under euxinic conditions[23,29], due to the rapid reduction of P-bearing Fe (oxyhydr)oxides by hydrogen sulphide[30,31], and the preferential release of P from decaying organic matter during sulphate reduction[21,23,29]. As a result, C:P ratios commonly surpass the canonical Redfield ratio of 106:1 by several orders of magnitude[21]. However, under all redox scenarios, some, or all, of the recycled phosphorus may be fixed in the sediment *via* the formation of authigenic phases during 'sink-switching', which involves the transfer of P from its carrier phase to a stable mineral form, such as authigenic apatite[29,32] or Fe phosphates (e.g., vivianite)[19,26–28].

An understanding of P recycling thus requires detailed analysis of both the phase partitioning of P, and the redox context in which P was transported to, and preserved in, ancient sediments. From ~1.8 Ga, oceans were generally characterised by oxygenated surface waters overlying mid-depth euxinic waters in productive regions, with ferruginous deeper waters[33–35]. Mid-depth water column euxinia would be expected to promote extensive P recycling to the water column from slope and shelf sediments[15], hence exerting a strong positive feedback on rates of primary production. Extensive euxinia in the mid-Proterozoic ocean contrasts sharply with the early Neoproterozoic (~1 to 0.8 Ga), where ferruginous conditions dominated the global ocean[8]. However, the response of the P cycle to this fundamental change in ocean redox chemistry has not been investigated.

Here, we quantify the speciation of P in ~1 to 0.9 Ga Neoproterozoic sediments from the Huainan basin (North China craton). We combine these data with C isotope systematics and existing Fe speciation data[8] to evaluate redox controls on P cycling and bioavailability. We subsequently incorporate constraints from Earth's surface redox balance and redox state to provide internally-consistent estimates of P, C_{org} and O_2 cycling under the globally-expansive ferruginous oceanic conditions of the early Neoproterozoic.

Geological setting

We focused on the ~1.0 to 0.9 Ga Liulaobei and Jiuliqiao formations (Huainan and Feishui Groups, Fig. 1), which represent unambiguously open marine continental margin successions covering a wide range of palaeodepths[8]. The Huainan Basin has experienced only low grade regional metamorphism[36], providing an ideal opportunity to explore the speciation of sedimentary P during the early Neoproterozoic. Full details of the geological setting are provided in Methods and Supplementary Information (SI).

Phosphorus drawdown in a ferruginous ocean

Iron speciation data for the succession shows strong evidence for persistent ferruginous water column conditions in the Huainan Basin[8], in agreement with the global signal from continental margin settings at this time[8,9]. Fe-bound phosphorus (P_{Fe}) constitutes the smallest P pool, representing on average ~5% of total P, despite the relatively high proportion of ferric oxides in our samples (Fig. S4). Organic P (P_{org}) is the second smallest contributor to total P (~9% on average). Authigenic carbonate fluorapatite (CFA) associated-P (P_{auth}), and detrital P (P_{det}) are the two largest P pools, representing an average of ~29% and ~58% of total P, respectively.

Under ferruginous conditions, the increased transport of P in association with Fe minerals can result in significantly higher sedimentary P/Al ratios[37]. Yet, in the persistently ferruginous Huainan Basin, sediment phosphorus (P_{Tot}) contents are low throughout the entire succession (Fig. 2). Normalised P/Al ratios are close to the average shale value of 0.009 (ref. 38), and show no evidence for P. These low P contents may reflect either a relatively low marine phosphate reservoir, which is faithfully recorded by the P preserved in the sediment, or a high degree of phosphorus recycling back to the water column during early diagenesis, which we explore further below.

Phosphorus cycling in the sediment

The extent to which P is released from organic matter and Fe (oxyhydr)oxides, and ultimately fixed in the sediment or recycled back to the water column, will likely depend on the C_{org} loading close to the sediment-water interface. This would affect rates of microbial organic matter degradation and the production of sulphide (and thus ultimately the release of P_{org} and P_{Fe}), at a depth in the sediment column where the P released could readily diffuse to the overlying water column.

The Huainan Basin sediments are characterised by low C_{org} (Fig. 2) and low pyrite concentrations, coupled with significant preservation of Fe (oxyhydr)oxide minerals (Fig. S4). This suggests that microbial recycling of C_{org} during early diagenesis was likely limited, and pore water chemistry at the sediment-water interface would have been poised at Fe reduction, rather than sulphate reduction. A lack of sulphide production close to the sediment-water interface would ultimately result in enhanced sedimentary P fixation, initially in association with Fe minerals and organic matter, followed by 'sink-switching' to other mineral phases such as authigenic apatite[32] or vivianite[37] deeper in the sediment profile. The speciation of P in our samples is consistent with these suggestions, whereby the relatively low P_{Fe} and P_{org} we observe relative to P_{auth} (Fig. 2) suggest significant ‘sink-switching’.

To further evaluate controls on P cycling, we consider variations in molar C_{org}:P_{org} ratios. Today, there is considerable variation between lower C_{org}:P_{org} ratios in nutrient replete conditions and higher C_{org}:P_{org} ratios in the most oligotrophic subtropical gyres (up to ~600; ref. 39). Consequently, it has been suggested that extreme P limitation in the mid-Proterozoic may have resulted in molar C_{org}:P_{org} ratios of up to 400 (ref. 12). Additionally, during incomplete remineralisation of C_{org}, preferential regeneration of P commonly results in higher C_{org}/P_{org} values[21,23,29]. For example, in laminated sediments underlying anoxic waters, C/P ratios may approach 600 in modern settings[21], and average at 3,900 in the geological record[40] (Table S2).

In our samples, C_{org}/P_{org} values are close to the Redfield ratio (Fig. 3A), reflecting little preferential loss of P from organic matter during deposition and early diagenesis. This is also supported by dominantly heavy carbonate-C isotope values (Fig. 2), as larger amounts of C_{org} mineralisation during diagenesis would potentially result in a wider range of (more) negative $\delta^{13}C_{carb}$ (ref. 41). C_{org}/P_{reac} rations (where P_{reac} represents potentially mobile P during deposition and early diagenesis; calculated as P_{org} + P_{auth} + P_{Fe}) also provide useful insight into controls on P cycling[32]. First, however, we consider whether our P_{det} analyses may have been affected by a possible transfer of authigenic apatite (i.e. P_{auth}) to the detrital apatite pool during burial diagenesis and metamorphism[42], which would lower primary P_{reac} values. We find strong linear relationships between P_{det} and Al (as a proxy for the detrital input) throughout the succession (see SI), which suggests that the measured P_{det} dominantly reflects the actual detrital P input, rather than post-depositional recrystallization. In support of these observations, we note that modern continental margin sediments typically have P_{det}

contents of 186 ± 21 ppm (ref. 32), which is somewhat higher than the average of 145 ± 89 ppm we observe for the Huainan Basin sediments. Furthermore, modern oligotrophic settings commonly have P_{det} values of 62-310 ppm (78 ± 41 ppm, ref. 27), which is similar to the range we observe (30-496 ppm). Hence, potential recrystallization of authigenic apatite was insignificant in terms of the dominant phase partitioning of phosphorus.

The molar ratios of C_{org}/P_{reac} plot below the Redfield ratio (Fig. 3A). Since we see little evidence for preferential release of P from organic matter, our novel C_{org}/P_{reac} approach therefore implies efficient drawdown of P from the ferruginous water column, presumably as Fe-bound P. While a small proportion of this original P_{Fe} was preserved, a significant proportion was ultimately fixed in the sediment as P_{auth}. This is consistent with high proportions of Fe_{carb} (Fig. S4), which likely formed during diagenesis following the dissolution of Fe minerals and release of adsorbed P.

An early Neoproterozoic oligotrophic ocean

The Huainan Basin sediments provide a case study for the behaviour of the P cycle under global ferruginous ocean conditions, and suggest that the low P content of these open ocean sediments reflects a relatively low seawater P reservoir in the early Neoproterozoic. This would have been a natural consequence of widespread P drawdown in association with Fe minerals as euxinia retracted and continental shelves transitioned to a ferruginous state[8]. A prediction of such conditions would be that sedimentary P should be dominated by detrital phosphorus[12], with some fixation of primary Fe-bound P as authigenic P, both of which we observe in the Huainan basin (Fig. 2). The development of a low seawater P reservoir would be expected to act as a limiting constraint on primary production. Indeed, C_{org}/P_{org} ratios close to the Redfield ratio, combined with lower C_{org}/P_{reac} ratios, are typical signatures of modern oligotrophic settings[27].

An alternative view to the 'Fe-bound phosphorus shuttle' as a driver for Precambrian ocean P limitation invokes decreased aerobic C_{org} remineralisation due to widespread ocean anoxia[43]. However, if a lack of aerobic recycling was responsible for low productivity throughout the Precambrian, then no significant change would be expected in the TOC loading of sediments as the redox structure of the anoxic ocean evolved from widespread euxinia to global ferruginous conditions. Although TOC contents are not a direct metric for the C_{org} flux to the sediment, there is, however, an apparent contrast between lower TOC contents in early Neoproterozoic shales and the preceding Mesoproterozoic[44] (see SI). This apparent contrast is entirely consistent with a mechanism invoking diminished C_{org} burial driven by a global decrease in productivity, due to efficient P removal and limited recycling under a global ferruginous state.

We can, however, provide a further, more direct test of this hypothesis *via* detailed investigation of euxinic sediments from the preceding mid-Proterozoic. We thus augment our data with ~1.1 Ga and ~1.8 Ga sediments deposited under euxinic conditions in the Taoudeni Basin (Mauritania) and the Animikie Basin (North America), respectively (see SI for sample descriptions and redox interpretations). In contrast to the ferruginous data, Figure 3B demonstrates extensive recycling of P from organic matter, in addition to efficient recycling of P back to the water column (C_{org}/P_{org} and C_{org}/P_{reac} are both significantly greater than the Redfield ratio), as we anticipated[15] under the euxinic conditions that characterised productive mid-Proterozoic continental margins[34,35]. Thus, when placed in the context of the global shale record (Fig. 4), the low P content of early Neoproterozoic sediments likely reflects low seawater P bioavailability under the global ferruginous conditions that occurred from ~1.0 to 0.8 Ga. This contrasts with the preceding mid-Proterozoic, where relatively low P contents instead reflect extensive recycling back to the water column under widespread euxinic conditions, resulting in a positive productivity feedback and hence increased C_{org} burial on a global scale (Fig. 5). However, despite an early Neoproterozoic drop in global productivity, sedimentary C_{org}:P_{org} ratios close to the Redfield ratio (Fig. 3A) suggest P limitation of primary production was not sufficiently extreme to alter phytoplankton stoichiometry.

Maintaining an oxidizing atmosphere

A recent model of Proterozoic atmospheric pO_2 regulation predicts a pO_2 of ~0.1 PAL during the Proterozoic, with a lower limit of pO_2 >0.01 PAL, below which O_2 is unstable and the GOE is reversed[45] (see SI for details on model assumptions). The sulphur cycle is estimated to have been a net sink for oxygen at ~1.0-0.9 Ga due to widespread gypsum evaporite deposition[8]. Hence, to maintain an oxidising atmosphere, the C_{org} burial flux must have exceeded the input flux of reduced gases (~1.25×10^{12} mol O_2 eq yr^{-1} in the present day, ref. 45). Comparing this to estimates of modern total (~5×10^{12} mol O_2 eq yr^{-1}) and marine (~2.5×10^{12} mol O_2 eq yr^{-1}) organic C burial, it suggests that Proterozoic C_{org} burial could not have fallen below ~25% of today's total value, or ~50% of today's marine value[45].

This constraint requires that reactive phosphorus inputs were at least half of today's value, and the global average C_{org}/P_{reac} burial ratio was comparable in magnitude to today. Our maximum total P contents of 0.05 wt% are comparable to the average value for upper continental crust[46] of 0.065 wt%, and the maximum TOC content of 0.3 wt% (Fig. 2) is comparable to today's reduced C content of upper continental crust and sediments of 0.4-0.6 wt%. Assuming our section is globally representative, a pre-anthropogenic sediment erosion rate of ~7 × 10^{15} g yr^{-1} (ref. 47) gives a total P burial flux of <1.1 × 10^{11} mol P yr^{-1}, and a P_{reac} burial flux of <4.6 × 10^{10} mol P yr^{-1} (using our average reactive P content of 42% total P), which is comparable to today's P weathering flux, estimated at ~4 (2.3-15.5) × 10^{10} mol P yr^{-1} (ref. 48). This gives a C_{org} burial flux of <1.75 × 10^{12} mol C yr^{-1}, which exceeds the ~1.25 × 10^{12} mol yr^{-1} threshold required to maintain an oxidising atmosphere (ref. 45). Thus, while efficient P removal under global ferruginous conditions drove a negative productivity feedback, we infer there was just sufficient C_{org} burial to maintain an oxidising atmosphere in the early Neoproterozoic.

Furthermore, the observation that the deep ocean was anoxic[49] implies that oxygen demand exceeded supply in deeper waters. During the early Neoproterozoic, which plausibly had a much weaker biological carbon pump, it would have been more difficult to drive deeper waters anoxic, requiring a pO_2/[PO_4] ratio <<0.4 of present levels[50]. Therefore, if pO_2 was >0.01 PAL, then [PO_4] >>0.025 of present ocean levels (POL) would be required, corresponding to [PO_4] >>0.055 μmol kg^{-1}. Alternatively, if pO_2 was ~0.1 PAL, then [PO_4] at >>0.25 POL (>0.55 μmol kg^{-1}) would be required to maintain deep ocean anoxia.

In summary, we infer that in the ferruginous early Neoproterozoic ocean, P was effectively removed from the water column and fixed in the sediment as authigenic phases. The lack of phosphorus regeneration into the water column likely constrained primary production and C_{org} burial, limiting the extent of atmospheric oxygen production. However, whilst the early Neoproterozoic had lower [PO_4] and pO_2 than the preceding late Paleo-Mesoproterozoic, our data and existing models suggest that the nature of P cycling supported sufficient C_{org} burial to maintain an oxidising atmosphere, with a stable pO_2 of >0.01 PAL, and $[PO_4]$ >>0.025 POL. Furthermore, sedimentary organic matter close to today's C_{org}/P_{org} Redfield ratio of ~106:1 argues against extreme P limitation of productivity. Together, these observations imply significant potential variability in atmospheric oxygen concentrations across Earth's 'middle age', which were tied to global-scale changes in ocean redox chemistry.

Data availability

All data generated and analysed for the current study are attached, and are available from data repository DOI:10.5285/72c9a48f-4813-4507-9137-a97d7e6bd2d9.

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Author contributions

R.G. and S.W.P. devised the research. R.G., S.W.P., G.A.S., Y.Z. and M.Z. collected the samples. J.T. and K.F.H. analysed the Mesoproterozoic samples. R.G. analyses the

Neoproterozoic samples and interpreted the data. R.G. wrote the manuscript, with significant contributions from all co-authors.

Financial and non-financial competing interests

The authors declare no competing interests.

Figure Captions

Figure 1. Sample locations within the north China craton.

a, Location of the Huainan Basin within the Rodinia supercontinent during the early Neoproterozoic. **b**, Huainan region location within modern day China. **c**, Sample locations (red stars) within the Huainan region in the Anhui province. The figure was modified after refs. (8,36).

Figure 2. Geochemical variations against the main stratigraphy of the Huainan Basin.

a, Stratigraphy of the Huainan Basin and lithology of the sections studied, modified after ref. (8). Geochemical variations include: **b**, Total organic carbon (TOC) and total Fe (Fe_T) contents; **c**, Organic carbon and carbonate carbon isotope compositions ($\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$, respectively); **d**, Total phosphorus (P_{tot}) contents and the P to aluminium ratio (P/Al), the dotted line representing the average shale value[38] (note the difference in x-axis); **e**, The proportion of detrital (P_{det}), authigenic (P_{auth}), organic-bond (P_{org}), and Fe oxide-bond (P_{Fe}) phosphorus within the total phosphorus pool. Errors are included within the data points.

Figure 3. Organic carbon (C) *versus* P (P) contents in Proterozoic sediments.

a, Molar organic C *versus* total P (P_{tot}), reactive P (P_{reac}) and organic-bound P (P_{org}) in the ferruginous Huainan Basin. **b**, Comparison with the ~1.1 Ga Taoudeni Basin, Mauritania (euxinic setting, represented by triangles) and the ~1.8 Ga Animikie Basin, North America (euxinic setting, represented by squares). The grey lines represent the Redfield C/P ratio of 106:1. C and P contents are given in mol per 100 g of sediment. Errors are included in the datapoints.

Figure 4. Phosphorus contents in black shales through time.

Compiled data of P contents in shales, plotted as grey circles, are from ref. 12. Data from the Huainan Basin (this study) are represented by closed red circles. The green boxes represent the whisker data for each associated time period. Compiled data were binned as a function of the time period considered, and the boxes represent the 1st quartile, median and 3rd quartile of the binned data. Whiskers mark the Tukey's range test for the binned data. Arrows indicate high value data in the Phanerozoic and the late Neoproterozoic that could not be represented on the figure.

Figure 5. Biogeochemical evolution of the ocean at the Mesoproterozoic-Neoproterozoic boundary (~1 Ga).

a, Prior to ~1 Ga, mid-depth, euxinic (sulphide-rich, H_2S) continental margins promoted phosphorous regeneration (as phosphate, PO_4^{3-}) through preferential release from organic carbon (C_{org}) and the reduction of Fe (oxyhydr)oxides, resulting in higher productivity and higher C_{org}-to-organic P (P_{org}) ratio. **b**, After ~1 Ga, under the globally ferruginous (Fe(II)-rich) early Neoproterozoic ocean, P was effectively removed from the water column and fixed in the sediment as authigenic phases through 'sink-switching', resulting in oligotrophic continental margins and C_{org}/P_{org} close to the Redfield ratio.

Methods

Geological context. The Huainan basin only witnessed low grade metamorphism, and hosts exceptionally well preserved, light-coloured acritarchs[36], as a result of low temperature gradients since deposition. Samples were collected from freshly exposed outcrops from an extensive, 700-800 m thick succession of shales, siltstones, mudstones and carbonates from the ~1-0.9 Ga Liulaobei and Jiuliqiao Formations. Because these sedimentary successions begin with relatively deep-water continental slope deposits, and shallow upwards to intertidal stromatolitic dolomites, they present an ideal site for exploring nutrient provision and cycling across a range of water depths.

TOC and C isotopes. TOC values are from a previously published study[8]. C isotope analyses were performed on the organic and carbonate fractions of the sediment samples. For the organic fraction, samples were decarbonated *via* two 24 h HCl washes (25% vol/vol), rinsed, centrifuged and dried before analysis. All data are reported with respect to the Vienna Pee Dee Belemnite standard (V-PDB), with a precision of ± 0.07‰ (1σ level).

Elemental analysis. Bulk sediment digestions were performed on ~50 mg of rock powder using HNO_3-HF-$HClO_4$ at ~70°C, followed by H_3BO_3 and HCl. Total P and Al contents were measured by ICP-OES, along with Mn and Sr, with a precision of ± 0.4 ppm for P and ± 0.9 ppm for Al, respectively ($n = 8$). Total digests of standard material

(PACS-2, National Research Council of Canada) yielded values within the certified range for all analyses elements (<3%).

P speciation. We performed the sequential phosphorus SEDEX extraction[51] adapted for ancient sedimentary rocks[25] (Table S2 and ref. 52) on sediment aliquots of ~150-200 mg. The method targets five operationally-defined phosphorus sedimentary pools, including iron bound phosphorus (P_{Fe}), authigenic CFA-associated P (P_{auth}), detrital apatite and inorganic P (P_{det}), organic bound P (P_{org}) and total P (P_{tot}). The applied method was slightly different to the SEDEX scheme, in that the "loosely sorbed P" step was omitted, and an additional HNO_3-HF-$HClO_4$-H_3BO_3-HCl extraction step (V) was performed on the residue in order to achieve near complete P recovery. Using this approach, an average recovery of 99% of the total P pool (as determined by ICP-OES) was achieved during the sequential extractions (Fig. S3-A). For each extraction step and washes, except for extraction step I, P concentrations were determined spectrophotometrically using the molybdate-blue method on a Spectonic GENESYS™ 6 at 880 nm. Reagents used in extraction I interfere with the molybdate complex, and for this step, P contents were measured by ICP-OES. Replicate analysis of a sample (n = 5) gave a RSD of <10% for each step, apart from P_{Fe}, where the RSD was 16%, partly due to the low concentrations of this phase (Table S2).

References only in Methods

51. Ruttenberg, K. C. Development of a sequential extraction method for different forms of phosphorus in marine sediments. *Limnology and Oceanography* **37**, 1460–1482 (1992).

52. Full data are available in the repository DOI: 10.0.20.165/72c9a48f-4813-4507-9137-a97d7e6bd2d9.