| 2 | activity in Svalbard | | | | | | |
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1 Neodymium isotope constraints on chemical weathering and past glacial

26 Abstract

27 Neodymium (Nd) isotopes in leached authigenic components of marine sediments have been 28 increasingly used as a tracer of past ocean-water masses. Despite the general assumption that the Nd 29 isotopic composition of solutes released during chemical weathering fingerprints the source rocks on 30 continents, preferential dissolution of easily dissolvable phases may result in significant deviations in 31 Nd isotopic composition between the solutes and the source rocks, with potential implications for the 32 utility of Nd isotopes in paleoenvironmental studies. Here, we present the Nd isotopic compositions of 33 leached and detrital fractions separated from bedrock and marine sediment samples from the Svalbard 34 archipelago. Our goal is to further understand the behaviour of Nd isotopes during chemical 35 weathering in glacial catchments and evaluate how glacier fluctuations and associated weathering 36 congruency may have affected the export of dissolved Nd isotope signatures to seawater.

37 Our results confirm that terrestrial weathering on Svalbard causes considerable Nd isotopic decoupling between the leached and detrital fractions of fjord sediments ($\Delta \varepsilon_{Nd}$), resulting from the 38 39 preferential dissolution of marine precipitates in glaciated catchments dominated by sedimentary 40 rocks. We also show that the degree of Nd isotopic decoupling has fluctuated in response to climate 41 variability on Svalbard during the Holocene, which is also as suggested by the occurrence of generally 42 higher $\Delta \varepsilon_{Nd}$ values during periods of glacier advances in sediment cores retrieved from two different 43 fjords (Dicksonfjorden and Woodfjorden). We posit that the high $\Delta \varepsilon_{Nd}$ values can be ascribed to 44 incongruent chemical weathering of fresh rock flour produced by glacial abrasion. This finding 45 suggests that the degree of Nd isotopic decoupling could be used as a new proxy for tracing glacial 46 fluctuations and associated glacier-derived nutrient inputs to the marine realm.

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Keywords: Neodymium isotopes, isotopic decoupling, incongruent weathering, glacier fluctuation,
Svalbard

1. Introduction

52 Global warming is having a profound impact on marine and terrestrial environments, and its 53 effects are particularly evident in polar regions, where glacier and sea-ice melting in combination with 54 associated changes in surface albedo and ocean heat distribution are key mechanisms underlying polar 55 amplification (Taylor et al., 2013 and references therein). Glacier melting and accompanying glacial 56 rock weathering have been recently identified as an important source of nanoparticulate nutrients 57 available for primary production in the ocean (Hawkings et al., 2015; Wadham et al., 2019), and they 58 potentially play an important role in marine biogeochemical cycles (review in Wadham et al., 2019). 59 However, the impact of glacier melting on nutrient releases and marine productivity relies on sparse 60 datasets (Hawkings et al., 2015). One important requirement for further evaluations of the future 61 relationship among climate changes, glacial weathering (understood as chemical weathering in glacial 62 catchments), glacier melting, and marine ecosystems is the reconstruction of past responses of glaciers 63 to climate and subsequent changes in meltwater discharge.

64 Neodymium (Nd) isotopes (often expressed using the ε_{Nd} notation) are widely used for 65 reconstructing past changes in ocean circulation and continental weathering fluxes (e.g., Bayon et al., 2002; Jang et al., 2017; Rutberg et al., 2000). A general consensus on the use of Nd isotopes in 66 67 paleoenvironmental studies is that negligible decoupling occurs during continental weathering and 68 sedimentary processes. However, in recent decades, multiple studies from river systems have shown 69 that preferential dissolution of labile phases relative to more resistant minerals during weathering 70 leads to markedly different Nd isotopic signatures in dissolved and solid loads (Goldstein and 71 Jacobsen, 1987), especially in sub-Arctic regions and glacier-covered areas (Andersson et al., 2001; 72 Hindshaw et al., 2018a; Süfke et al., 2019). This evidence for decoupling of Nd isotopes in the glacial 73 environment suggests that past episodes of glacial retreats and advances could have possibly affected 74 the ε_{Nd} signatures of the dissolved loads exported to the ocean over centennial to millennial time 75 scales in high-latitude regions (Hindshaw et al., 2018a). For instance, an increased supply of fresh 76 rock substrates by glacial abrasion could have led to enhanced incongruent weathering on continents 77 (Vance et al., 2009), which would have resulted in greater Nd isotopic decoupling during past cold

78 events because of the intrinsic Nd isotopic differences in rock-forming minerals. The importance of 79 Nd isotopes in provenance studies and their utility for tracing past meltwater releases call for a better 80 understanding of their behaviour during glacial weathering and further evaluation of how past glacial 81 dynamics may have influenced the isotopic composition of dissolved Nd exported to the ocean. 82 In this study, we present an extensive set of Nd isotopic compositions measured in both 83 labile and detrital fractions of a series of sedimentary and metamorphic rock samples and surface 84 sediment samples from across the Svalbard archipelago. Our aim is to characterize the effect of 85 incongruent silicate weathering on Nd isotopes. Two marine sediment cores from fjords covering the 86 Holocene period were also analyzed to assess the impact of past glacial advances and retreats on Nd 87 isotopic decoupling and the preservation of ε_{Nd} signatures by surrounding water masses. The Svalbard 88 archipelago is largely covered by glaciers and has diverse bedrock compositions, including 89 sedimentary, metamorphic and volcanic rocks (Dallmann and Elvevold, 2015). Thus, the area is well

suited for investigating the behaviour of Nd isotopes during glacial weathering.

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90

92 2. Background

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2.1. Nd isotope behaviour during weathering

94 Easily dissolvable components in rocks and sediments, such as marine precipitates (e.g., bio-95 skeletal carbonates, phosphates and Fe-Mn oxides) and labile detrital minerals (e.g., volcanic 96 components and accessory minerals) (Goldstein and Jacobsen, 1987; Hindshaw et al., 2018a), can be 97 selectively extracted using chemical leaching methods (Bayon et al., 2002; Gutjahr et al., 2007). The comparison of radiogenic isotopic compositions between 'leachable' and residual silicate phases 98 99 indicates whether isotopic decoupling may occur during continental weathering (e.g., Dausmann et 100 al., 2019). A recent experimental investigation of Nd isotopes conducted on Svalbard (Dryadbreen and 101 Fardalen river basins; Fig. 1) clearly showed that bedrock leachates and river waters presented more 102 radiogenic Nd isotopic values (= higher ε_{Nd}) than the parent bedrocks (Hindshaw et al., 2018a), 103 suggesting that the isotopic composition of dissolved Nd is controlled by the preferential dissolution 104 of labile phases during weathering. While such decoupling is mostly observed in sedimentary

105 catchments (Goldstein and Jacobsen, 1987), where radiogenic labile components typically occur as 106 marine precipitates (e.g., Hindshaw et al., 2018a), preferential dissolution of easily dissolvable 107 accessory minerals such as apatite or titanite, can also result in decoupling in granitic catchments 108 (e.g., Dausmann et al., 2019; Süfke et al., 2019). 109 On continents, the extent or magnitude of incongruent weathering is considered to be 110 climate-dependent (Vance et al., 2009). Enhanced incongruent weathering of glacially eroded rock 111 substrates is generally thought to have occurred during past cold periods, and they most likely resulted 112 in an intensified release of radiogenic Nd and Pb isotopes into dissolved river loads and the marine environment. This process has been inferred in part on the basis of pronounced radiogenic Pb isotope 113 114 excursions in various late Quaternary sediment records of dispersed Fe-Mn oxyhydroxide phases from 115 the North Atlantic (Gutjahr et al., 2009) and high Alpine lake sediments (Süfke et al., 2019). 116 Furthermore, Süfke et al. (2019) documented a trend towards more radiogenic authigenic Nd isotopic values in an Alpine lake sediment record, suggesting that Nd isotopes could also record enhanced 117 118 incongruent weathering of glacially derived material in the past. Similarly, long-term variations in Pb 119 and Nd isotopes in North Atlantic ferromanganese crusts across the onset of Northern Hemisphere glaciations have also been attributed to changes from chemical- to physical-dominated weathering 120 regimes on surrounding continents (Gutjahr et al., 2009; von Blanckenburg and Nägler, 2001). 121 122 2.2. 123 Study area

124 This study is based on bedrock samples from multiple onshore locations as well as sediment 125 samples from various fjords on Spitsbergen, the largest island of the Svalbard archipelago (Fig. 1). 126 The Svalbard archipelago is located between approximately 74-81°N and 10-35°E and surrounded by 127 the Barents Sea and the Greenland Sea (Fig. 1). Three main water masses contribute to the 128 hydrography of Spitsbergen fjords: (1) relatively warm and saline Atlantic Water (AW; T > 3.0 and S 129 > 34.65; Cottier et al., 2005 and references therein) carried by the West Spitsbergen Current (WSC; 130 Fig. 1), (2) cold and relatively fresh Arctic water (ArW; -1.5 < T < 1 and 34.3 < S < 34.8; Cottier et 131 al., 2005 and references therein) by the Sørkapp Current, an extension of the East Spitsbergen Current 132 (ESC; Fig. 1), and (3) glacial meltwater (Cottier et al., 2005). Their mixing varies depending on 133 location within a fjord, water depth, and season of a year, resulting in complex hydrography 134 containing various water masses such as Surface Water (SW), Local Water (LW), Intermediate Water 135 (IW), Transformed Atlantic Water (TAW), and Winter Cooled Water (WCW) (e.g., Promińska et al., 136 2017; Zajączkowski et al., 2010). A top-most layer in late spring and summer is occupied by fresh SW (S < 34.00), which is strongly affected by glacial meltwater. LW (34.30 < S < 34.85, -0.5 < T < 100137 1.0) and WCW (T < -0.5, 34.40 < S < 35.00) are formed by surface cooling during autumn and brine 138 139 formation during winter, respectively, while TAW ($1.0 \le T \le 3.0, 34.65 \le S$) and IW ($34.00 \le S \le 10^{-5}$) 34.65, T > 1.0) are formed by mixing between AW and ArW, as well as various fjord masses (Cottier 140 141 et al., 2005).

142 The bedrock geology of Svalbard in general as well as in the catchment areas of the studied fjords, is very diverse and ranges from Proterozoic metamorphic rocks to Phanerozoic sedimentary 143 rocks (Dallmann and Elvevold, 2015) (Fig. 2). Hornsund is dominated by Proterozoic metamorphic 144 145 rocks at the fjord mouth in the west to Palaeogene sedimentary rocks at the fjord head in the east. 146 They display complicated structures, including folds, faults, and overthrusts (Dallmann and Elvevold, 2015). Similarly, the Van Mijenfjorden and Isfjorden systems display the longitudinal (W-E) 147 variability in bedrock geology from Proterozoic metamorphic rocks to Carboniferous to Palaeogene 148 149 sedimentary rocks. The catchment area of Dicksonfjorden, a northern tributary of Isfjorden, is 150 composed of sedimentary sequences, including Devonian Old Red Sandstones and siltstones and 151 Carboniferous-Permian carbonate-siliciclastic strata. The catchment area of Woodfjorden primarily 152 consists of the Devonian Old Red Sandstone with a minor Quaternary volcanic complex, and 153 Mesoproterozoic metamorphic and igneous rocks located at the heads of its tributaries (Fig. 2). The 154 catchment of Wijdefjorden is dominated by Proterozoic to lower Silurian metamorphic rocks along 155 the eastern shore and Upper Silurian to Devonian sedimentary rocks in the west (Dallmann and 156 Elvevold, 2015).

157 During the Holocene, Svalbard experienced several phases of glacier advances and retreats.
158 The deglaciation of the inner fjords of west Spitsbergen terminated approximately 11.2 ka (Baeten et

| 159 | al., 2010; Forwick and Vorren, 2009), and a warming period in western Spitsbergen lasted until 9 to 8 |
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| 160 | ka (Forwick and Vorren, 2009; Rasmussen et al., 2012). Gradual cooling accentuated by several |
| 161 | asynchronous cooling steps (e.g., Rasmussen et al., 2012) followed this period (Forwick and Vorren, |
| 162 | 2009). In particular, the enhanced growth and/or reformation of glaciers (Fjeldskaar et al., 2018), such |
| 163 | as Linnébreen, Nordenskiöldbreen, Tunabreen and those in the Hajeren lake catchment occurred |
| 164 | between 6 and 4 ka (Baeten et al., 2010; Forwick et al., 2010; Svendsen and Mangerud, 1997; van der |
| 165 | Bilt et al., 2015). Most glaciers reached their maximum Holocene extents during the Little Ice Age |
| 166 | (LIA) (~66 % with a total area of 38,871 km ² ; Martín-Moreno et al., 2017). Glaciers have been |
| 167 | retreating since the termination of the LIA, and approximately 57% of Svalbard is currently covered |
| 168 | with glaciers (total area of 33,775 km ² ; Martín-Moreno et al., 2017 and references therein). |
| 169 | The study focuses in particular on the analysis of two sediment cores from Dicksonfjorden |
| 170 | and Woodfjorden. The sediment supply to Dicksonfjorden occurs mainly by glacio-fluvial runoff. On |
| | |
| 171 | the other hand, the main sediment sources in Woodfjorden are glacio-fluvial rivers in inner |
| 171 172 | the other hand, the main sediment sources in Woodfjorden are glacio-fluvial rivers in inner Woodfjorden and Bockfjorden as well as tidewater glaciers in Liefdefjorden. At present, WCW forms |
| 171 172 173 | the other hand, the main sediment sources in Woodfjorden are glacio-fluvial rivers in inner Woodfjorden and Bockfjorden as well as tidewater glaciers in Liefdefjorden. At present, WCW forms by convection during the fall and winter seasons in both fjords. However, considering the known past |
| 171 172 173 174 | the other hand, the main sediment sources in Woodfjorden are glacio-fluvial rivers in inner Woodfjorden and Bockfjorden as well as tidewater glaciers in Liefdefjorden. At present, WCW forms by convection during the fall and winter seasons in both fjords. However, considering the known past climate and glacier variations in Svalbard during the Holocene (Baeten et al., 2010; Rasmussen et al., |
| 171 172 173 174 175 | the other hand, the main sediment sources in Woodfjorden are glacio-fluvial rivers in inner Woodfjorden and Bockfjorden as well as tidewater glaciers in Liefdefjorden. At present, WCW forms by convection during the fall and winter seasons in both fjords. However, considering the known past climate and glacier variations in Svalbard during the Holocene (Baeten et al., 2010; Rasmussen et al., 2012; Svendsen and Mangerud, 1997), the oceanographic and sedimentary regime were different in |
| 171 172 173 174 175 176 | the other hand, the main sediment sources in Woodfjorden are glacio-fluvial rivers in inner Woodfjorden and Bockfjorden as well as tidewater glaciers in Liefdefjorden. At present, WCW forms by convection during the fall and winter seasons in both fjords. However, considering the known past climate and glacier variations in Svalbard during the Holocene (Baeten et al., 2010; Rasmussen et al., 2012; Svendsen and Mangerud, 1997), the oceanographic and sedimentary regime were different in the past. The relative sea level fell by up to 65 m on Spitsbergen during the last 12 ka (Forman et al., |
| 171 172 173 174 175 176 177 | the other hand, the main sediment sources in Woodfjorden are glacio-fluvial rivers in inner Woodfjorden and Bockfjorden as well as tidewater glaciers in Liefdefjorden. At present, WCW forms by convection during the fall and winter seasons in both fjords. However, considering the known past climate and glacier variations in Svalbard during the Holocene (Baeten et al., 2010; Rasmussen et al., 2012; Svendsen and Mangerud, 1997), the oceanographic and sedimentary regime were different in the past. The relative sea level fell by up to 65 m on Spitsbergen during the last 12 ka (Forman et al., 2004). The most pronounced changes occurred at the end and shortly after the deglaciation, and only |
| 171 172 173 174 175 176 177 178 | the other hand, the main sediment sources in Woodfjorden are glacio-fluvial rivers in inner Woodfjorden and Bockfjorden as well as tidewater glaciers in Liefdefjorden. At present, WCW forms by convection during the fall and winter seasons in both fjords. However, considering the known past climate and glacier variations in Svalbard during the Holocene (Baeten et al., 2010; Rasmussen et al., 2012; Svendsen and Mangerud, 1997), the oceanographic and sedimentary regime were different in the past. The relative sea level fell by up to 65 m on Spitsbergen during the last 12 ka (Forman et al., 2004). The most pronounced changes occurred at the end and shortly after the deglaciation, and only minor changes have occurred since the middle Holocene. |

- 179
- 180 **3.**

Materials and methods

181 *3.1. Materials*

182 *3.1.1.* Bedrock

183 A total of 18 fresh unweathered rock samples from representative bedrock units of Svalbard

184 were collected (Isfjorden, n = 10; Kongsfjorden, n = 7; Woodfjorden, n = 1; Table 1 and Fig. 2).

185 Metamorphic rocks (i.e., quartzite and phyllite) were collected from the upper Proterozoic

Generalfjella Formation in the Kongsfjorden area, while sandstone samples were collected from
Isfjorden, Billefjorden and Woodfjorden. The Woodfjorden sandstone corresponds to the Devonian
Old Red Sandstone, which represents the main source of sediments in Dicksonfjorden and inner
Woodfjorden. Carboniferous bedrock samples from the Kongsfjorden and Isfjorden areas are mainly
composed of calcareous sedimentary rocks (limestone and dolostone), while the Mesozoic bedrock
samples from Isfjorden include siliciclastic mudstones, siltstones, and sandstones.

192

193 *3.1.2.* Surface sediments

A total of 45 surface (0-1 cm sediment depth) and sub-surface sediment samples (up to 5-6 194 195 cm sediment depth) (hereafter, surface sediments) from Bockfjorden (n = 1), Dicksonfjorden (n = 8), 196 Hornsund (n = 21), Liefjefjorden (n = 1), Tempelfjorden (n = 1), Van Mijenfjorden (n = 2), 197 Wijdefjorden (n = 8) and Woodfjorden (n = 2) (Fig. 3) were collected to characterize the modern distribution of sedimentary Nd isotopes in Spitsbergen fjords. The material was retrieved with a giant 198 199 box corer $(50 \times 50 \times 50 \text{ cm}^3)$ or a gravity corer during cruises of the *RV Helmer Hanssen* of UiT The 200 Arctic University of Norway in 2012, 2015, 2016, and 2017 (Supplementary Table S1). The sampling sites are located at water depths ranging from 37 to 322 m, and they are in contact with the water 201 202 masses mentioned earlier (section 2.2) depending on the fjord location, water depth and distance from 203 the fjord mouth (e.g., Promińska et al., 2017; Zajączkowski et al., 2010).

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205 3.1.3. Core sediments

Two gravity cores from Dicksonfjorden (HH16-1202-GC; 78.727°N, 15.310°E, ~87 m water depth) and Woodfjorden (HH12-964-GC; 79.651°N, 13.755°E, ~173 m water depth) were retrieved to reconstruct the evolution of sedimentary Nd isotopic compositions during the Holocene. Core HH16-1202-GC is ~274 cm long and spans the last 8.2 ka (Joo et al., 2019), with an average sediment accumulation rate of ~33 cm/ka. The lithology is dominated by reddish-brown mud that includes varying amounts of sandy detrital clasts. Core HH12-964-GC is ~334 cm long and spans the last ~13.3 ka (Hansen, 2014). The average sediment accumulation rate is 25.1 cm/ka, although rates of up to 91 cm/ka were calculated for the lower parts of the core. The lithology of core HH12-964-GC is dominated by silt-sized sediment, with the occurrence of coarser intervals at ~110 cm and near the bottom of the core (Hansen, 2014). In each core, 1 cm thick sediment layers were collected at 10 cm intervals for the Nd isotope analyses (n = 28 for HH16-1202-GC and n = 35 for HH12-964-GC).

218 *3.2. Analytical methods*

219 *3.2.1.* Sample preparation

220 In this study, we define 'authigenic' and 'weatherable' components as the easily dissolvable fractions (e.g., carbonate, and Fe-Mn oxyhydroxide) extracted by chemical leaching from unwashed 221 222 ground bulk sediments and from bedrock, respectively (Bayon et al., 2002; Gutjahr et al., 2007; Jang 223 et al., 2017; Rutberg et al., 2000; Werner et al., 2014). The protocol used for chemical leaching is based on the addition of 0.02 M hydroxylamine hydrochloride in 25% acetic acid buffered to pH ~4 224 using NH₄OH (hereafter, HH solution) for less than 1 hour (Jang et al., 2017). The reagent-to-sample 225 226 volume ratio was approximately 1 (Jang et al., 2017) to prevent the dissolution of labile detrital 227 components (e.g., volcanic material) during the leaching process. Following the extraction of the 228 authigenic and/or weatherable components, a second leaching step was carried out using the HH 229 solution for ~24 hours to eliminate any remaining carbonate or Fe-Mn oxyhydroxide materials from 230 the residual 'detrital' fraction (Jang et al., 2017).

231 After rinsing with Milli-Q water (Millipore, >18.2 M Ω cm), the detrital fractions were 232 digested by alkaline fusion for Nd isotopic measurements (Bayon et al., 2009). Approximately 100 mg 233 of dry ground detrital sediment was transferred into a glassy carbon beaker (SIGRADUR GAB 3, 234 HTW) with 1.2 g of Na₂O₂ (>95%, small beads, ACS grade, Sigma-Aldrich) and 0.6 g of NaOH 235 (>98.0%, pellet, ACS grade, Sigma-Aldrich) and placed in a furnace at ~700°C for ~15 min. 236 Neodymium and other reactive elements were then co-precipitated onto Fe oxide phases after the 237 addition of ultrapure Milli-Q water. After centrifugation, Fe oxide precipitates were rinsed in Milli-Q

238 water and dissolved in 2 M HNO₃. Neodymium was purified by ion chromatography following a

protocol modified from Pin and Zalduegui (1997) (Jang et al., 2017).

241 *3.2.2.* Elemental concentration analysis

242 The elemental abundances (Al, K, Ca, Mg, Fe, and rare earth elements (REEs)) of whole-243 rock samples and detrital fractions were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, OPTIMA 8300, PerkinElmer) and mass spectrometry (ICP-MS, Thermo X-244 245 5, Thermo Scientific) at the Korea Basic Science Institute (KBSI). Prior to the elemental analyses, the samples were dissolved by acid digestion in a PTFA digestion vessel using a 4:4:1 mixture of HNO₃, 246 HF, and HClO₄. Repeated analyses of USGS rock reference powders (BCR-2 and BHVO-2) yielded a 247 reproducibility better than $\pm 5\%$ (1 σ , standard deviation). 248 249 3.2.3. Nd isotope analyses 250 Neodymium isotopic measurements were performed by thermal ionization mass 251 spectrometry (TIMS, Triton, Thermo Scientific) at the Korea Polar Research Institute. All measured 252 ratios were corrected for mass fractionation using $^{146}Nd/^{144}Nd = 0.7219$. Repeated analyses of JNdi-1 253 standard solutions yielded an average value of 143 Nd/ 144 Nd = 0.512100 ± 0.000011 (2 σ , n = 30), which 254 were consistent with the reference value (0.512115) of Tanaka et al. (2000). The validity of the 255 analytical procedure was further evaluated by analyzing the USGS reference materials BCR-2 256 257 $(0.512631 \pm 0.000013, 2\sigma, n = 3)$ and BHVO-1 $(0.512975 \pm 0.000009, 2\sigma, n = 3)$, which were also consistent with values from the literature (e.g., Raczek et al., 2003). The total procedure blank was 258 259 < 0.2% Nd for the detrital fractions and an order of magnitude less for the leached authigenic phases. In this study, Nd isotopic ratios are reported using the epsilon notation (ε_{Nd}), which represents the 260 deviation of any measured ¹⁴³Nd/¹⁴⁴Nd ratio relative to the value for the modern chondritic uniform 261 reservoir ($(^{143}Nd/^{144}Nd)_{CHUR} = 0.512638$; Jacobsen and Wasserburg, 1980). 262 263 264 4. **Results**

265 4.1. Svalbard bedrocks

Elemental and isotopic data for the detrital and weatherable fractions of the bedrock samples

267 (n = 18) are reported in Supplementary Table S2, Table 1, and Fig. 2. The Nd concentrations in these 268 samples vary from ~0.3 to ~43 mg/kg for the bulk samples and from ~0.03 to ~33 mg/kg for the 269 detrital components. Limestone, dolostone, and anhydrite are characterized by much lower Nd 270 concentrations (0.3 to 4.0 mg/kg for bulk samples) compared with those in the siliceous sedimentary 271 rocks, such as the Devonian Old Red Sandstone and the Permian black mudstone (up to ~43 mg/kg 272 for bulk and ~35 mg/kg for the detrital component).

273 The detrital and weatherable fractions of the bedrocks display wide ranges of ε_{Nd} values, 274 from -25.9 to 3.4 and from -25.6 to -1.2, respectively (Fig. 2). The average values of detrital and weatherable ε_{Nd} are -9.8 ± 6.6 (1σ , n = 14) and -9.8 ± 5.7 (1σ , n = 15), respectively, and the two 275 276 isotopic compositions are strongly correlated with each other (r = 0.82, n = 14). The Cretaceous 277 sandstone and the mid-Jurassic to early Cretaceous shale collected close to the mouth of Isfjorden presented the minimum ε_{Nd} value (-25.9 for detrital and -25.6 for weatherable) and maximum ε_{Nd} 278 value (+3.4 for detrital and -1.2 for weatherable) measured in the bedrocks. Note that analyses of Nd-279 280 poor bedrocks, such as anhydrite (< 0.4 mg/kg for bulk), limestone (< 4 mg/kg for bulk) and two 281 dolostone samples (< 1.3 mg/kg for bulk), were not possible due to insufficient intensity signals 282 during the TIMS analysis. Except for the Cretaceous sandstone and the upper Proterozoic phyllite, the 283 Nd isotopic compositions of the weatherable fractions are statistically different from the 284 corresponding detrital fractions. Except for three Mesozoic shales, the weatherable ε_{Nd} signatures are systematically more radiogenic (up to 5 epsilon-units higher) than the corresponding detrital fractions 285 286 (Figs. 3 & 4).

287

288 4.2. Fjord surface sediments

The Nd concentrations of the bulk samples and their detrital components of the surface sediments show average values of 48 and 40 mg/kg, respectively. Thus, they are higher than the maximum concentrations reported for the bedrock samples (see *section 4.1*). The ε_{Nd} compositions of the detrital components range from -24.9 to -10.1 (with an average of -14.7 ± 3.0; 1 σ , n = 45), while those of the authigenic components are more radiogenic, ranging from -14.5 to -9.0 (with an average 294 of -11.5 \pm 1.5; 1 σ , n = 45) (Figs. 3 & 4). The correlation between the detrital and authigenic ε_{Nd} is 295 strong (r = 0.62) but not as strong as that of the bedrock. Note that the sediments collected from 296 Hornsund, with average detrital and authigenic ε_{Nd} values of -15.1 ± 3.0 and -10.8 ± 1.5 (1 σ , n = 21), 297 respectively, display a large spatial variability reflecting the presence of various bedrock types in the surrounding catchment area, including Proterozoic metamorphic rocks and Palaeozoic, Mesozoic and 298 299 Palaeogene sedimentary sequences (Dallmann and Elvevold, 2015). The sediments recovered from 300 Dicksonfjorden are comparatively uniform in terms of Nd isotopes, with average detrital and 301 authigenic ε_{Nd} values of -13.6 \pm 0.1 and -11.5 \pm 0.2 (1 σ , n = 8), respectively, which are very similar to the composition of the Devonian Old Red Sandstone (-13.6 \pm 0.3 and -10.8 \pm 0.2, respectively). 302 303 Similar detrital ε_{Nd} values were also obtained for sediments from Woodfjorden and its tributary fjords $(-13.6 \pm 0.5, 1\sigma, n = 4)$. However, the elemental ratios (e.g., Fe/Ca and Ca/Al; Supplementary Table 304 S3) and sediment colours are different from that in Dicksonfjorden. In Wijdefjorden, the detrital ε_{Nd} 305 values of surface sediments are between those of the Devonian Old Red Sandstone (-13.6 \pm 0.3) 306 307 collected from the Woodfjorden catchments (Fig. 2B) and Paleoproterozoic meta-igneous rocks from 308 Ny-Friesland ($\epsilon_{Nd} \sim -25.4$ to -18.6 from Johansson et al., 1995) (Fig. 2A). The sediments collected in 309 Van Mijenfjorden are characterized by less radiogenic detrital ε_{Nd} values of -17.3 and -16.9.

310

311 *4.3.* Core sediments

312 4.3.1. Dicksonfjorden

313 Sediments at site HH16-1202 in Dicksonfjorden are characterized by detrital and authigenic 314 ϵ_{Nd} values ranging from -14.5 to -12.9 (average -13.5 \pm 0.3, 1 σ , n = 28), and from -11.5 to -10.4 315 (average -11.2 ± 0.2), respectively (Fig. 5). Compared with the bedrock and core-top sediment 316 samples, the detrital and authigenic ε_{Nd} values at site HH16-1202 display only a moderate correlation over the past 7.6 ka (r = 0.43, n = 28). Some ε_{Nd} excursions can be detected in the core for both 317 318 detrital and authigenic fractions (e.g., the more radiogenic value at ~3.5 ka) as well as only for the detrital (less radiogenic ϵ_{Nd} shifts during the last millennia) or authigenic fractions (e.g., more 319 radiogenic authigenic value at ~4.5 ka). 320

322 4.3.2. Woodfjorden

| 323 | The detrital ε_{Nd} values at site HH12-964 in Woodfjorden fluctuated from -14.5 to -8.7 over |
|-----|--|
| 324 | the last 13.3 ka (Fig. 6), whereas the authigenic fractions displayed a much narrower range of ϵ_{Nd} |
| 325 | signatures (from -11.8 to -10.6; average value -11.2 \pm 0.3, 1 σ , n = 35) (Fig. 6). For the detrital |
| 326 | fractions, the average ϵ_{Nd} value of -13.4 is consistent with that of the Devonian Old Red Sandstone. |
| 327 | Prominent peaks in the detrital ε_{Nd} values towards radiogenic signatures occurred at ~7.2 ka and ~13.2 |
| 328 | ka. The overall downcore trend of authigenic values ϵ_{Nd} does not correlate with that of the detrital ϵ_{Nd} |
| 329 | values ($r = -0.07$), which is probably due to several outliers in the detrital ε_{Nd} trend. |

330

331 **5. Discussion**

332 5.1. Nd isotopic decoupling during incongruent terrestrial weathering in Svalbard

The weatherable components extracted from the analyzed bedrocks usually display more 333 334 radiogenic Nd isotopic compositions than the corresponding detrital silicate fractions (Figs. 3 & 4). 335 Enriched radiogenic Nd isotope ratios of leachates could be found, such as in volcanogenic sediments 336 (e.g., Elmore et al., 2011). However, we are confident that the observed radiogenic Nd isotopic 337 composition in the weatherable fraction does not result from the preferential dissolution of labile 338 volcanic components due to four reasons (Supplementary Text 1). First, our mild leaching procedure would have prevented any significant detrital contamination (Jang et al., 2017). Second, if significant 339 340 detrital contamination had occurred, then preferential leaching of the volcanogenic sediment in core HH12-964 should have occurred, which would have yielded pronounced radiogenic signatures in the 341 leached authigenic fractions (which is not the case). Third, the authigenic ε_{Nd} signature at site HH17-342 1086 in Wijdefjorden (Fig. 1) is statistically consistent with the neighbouring seawater ε_{Nd} (see more 343 344 detail in section 5.2.1). Finally, although the sediments collected from two proximal sites in Hornsund 345 display similar detrital ε_{Nd} and major element geochemistry, they present different authigenic ε_{Nd} 346 values, which is consistent with their overlying bottom water masses showing contrasting water 347 temperatures (see more detail in section 5.2.2).

348 As a consequence, the observed Nd isotopic decoupling between the weatherable and detrital 349 components of Svalbard bedrocks is most likely best explained by the preferential dissolution of 350 marine precipitates hosted by sedimentary rocks and/or labile accessory mineral phases in silicate 351 rocks. The same hypothesis was recently proposed by Hindshaw et al. (2018a) to account for the 352 observation that dissolved riverine loads in Svalbard were more radiogenic than corresponding 353 suspended sediments, bedrocks, and glacial sediments (Fig. 4). In full agreement with this finding, our 354 rock leaching experiments demonstrate that incongruent weathering in Svalbard can lead to 355 significant Nd isotopic decoupling (Supplementary Text 2). Sedimentary rocks consist of various biogenic and authigenic components that are generally admixed with older recycled detrital minerals 356 357 derived from the erosion of the basement and presumably characterized by less radiogenic ε_{Nd} 358 compositions (e.g., Hindshaw et al., 2018b).

Previous studies have also reported pronounced Nd isotopic differences between dissolved loads and suspended sediments or bedrocks in catchments (Andersson et al., 2001; Goldstein and Jacobsen, 1987), particularly in sub-arctic river systems draining old metamorphic rocks (Andersson et al., 2001). Preferential alteration of easily dissolvable and radiogenic accessory minerals, such as apatite or titanite, is likely to occur during the weathering of igneous and metamorphic rocks (e.g., Andersson et al., 2001; von Blanckenburg and Nägler, 2001) as demonstrated by the rock leaching experiments (Dausmann et al., 2019).

In this study, significant Nd isotopic decoupling between detrital and weatherable fractions 366 367 (> 1.2 epsilon-units) was observed in one of the two metamorphic rock samples and 11 of the 12 368 sedimentary rock samples, with the most pronounced isotopic decoupling (about 9 epsilon-units) 369 occurring in the Carboniferous sandstone (Figs. 3 & 4). Interestingly, the ε_{Nd} differences between the 370 weatherable and detrital fractions in sedimentary rocks were not always positive and presented 371 negative values in four samples (Figs. 3 & 4). This finding contradicts the common assumption that 372 incongruent weathering leads to the release of more radiogenic Nd fractions compared to residual 373 detrital fractions (Andersson et al., 2001; Dausmann et al., 2019; Goldstein and Jacobsen, 1987; 374 Hindshaw et al., 2018a; von Blanckenburg and Nägler, 2001). The negative ε_{Nd} offsets were found in 375 the Carboniferous sandstone (with a Nd isotopic difference of -9 epsilon-units) and three Mesozoic 376 shale samples (with ε_{Nd} differences between -3.0 and -4.6 epsilon-units); thus, in these samples, the 377 detrital ε_{Nd} values are comparatively more radiogenic than the weatherable ε_{Nd} values. The presence of 378 abundant radiogenic mineral phases, such as zircon or garnet (characterized by high Sm/Nd ratios; see 379 Fig. 2 in Bayon et al., 2006), in silicate residual phases could account for the observed ε_{Nd} differences 380 between the weatherable and detrital fractions. However, it is also likely that these negative ε_{Nd} 381 differences reflect the fact that detrital fractions in sedimentary rocks may have been derived from the 382 erosion of silicate bedrocks that are more radiogenic than associated weatherable marine precipitates.

383

384 5.2. Origin of the authigenic ε_{Nd} in Svalbard fjord sediments

385 *5.2.1.* Terrestrial signals

The strong Nd isotope correlation (r = 0.62) observed between authigenic and detrital 386 387 fractions of Svalbard fjord sediments suggests that the ε_{Nd} signature of leached phases is mainly 388 influenced by terrestrial inputs (Fig. 4). As reported previously, the presence of preformed Fe oxides 389 delivered together with detrital inputs could at least partially account for these 'terrestrial' ε_{Nd} 390 signatures (Bayon et al., 2004; Werner et al., 2014). Such preformed terrestrial Fe oxides can be 391 entrained in sea-ice (Werner et al., 2014) or delivered via riverine inputs (Bayon et al., 2004). 392 However, preformed Fe oxides do not account for the characteristic features of authigenic ε_{Nd} 393 described in section 5.2.2.

394 Alternatively, glacial meltwater runoff to the fjords through glacial rivers or direct outflows 395 from tidewater glaciers is known to deliver substantial amounts of dissolved and nanoparticulate iron 396 (Poulton and Raiswell, 2005; Wadham et al., 2019; Wehrmann et al., 2014), and this is also the case 397 for Svalbard, where large inputs of dissolved iron and Fe oxides can occur as a result of the glacial 398 abrasion and subsequent dissolution of silicate rocks or iron-bearing sedimentary rocks (Hindshaw et 399 al., 2018a; Wehrmann et al., 2014). This mechanism can be further promoted in polar regions by the 400 photoreductive dissolution of Fe oxides trapped in ice (Kim et al., 2010). In Svalbard, this process 401 may be linked to markedly higher contents of highly reactive Fe oxides observed in fine-grained

glacial meltwater sediments in Finsterwalderbreen compared to other glacial and riverine sediments in
the world (Poulton and Raiswell, 2005). Iron oxide in such sediments is mainly hosted by clay-bound
nanoparticulate Fe oxides (10-20 nm diameter) (Poulton and Raiswell, 2005), which can be easily
dissolved in seawater (Moore et al., 1979), hence representing a potential source of dissolved iron
(and presumably REEs) for subsequent authigenic Fe-oxyhydroxide co-precipitation in Svalbard
fjords.

408 Vertical benthic fluxes related to the early diagenetic iron cycle in marine sediments 409 represent another substantial source of dissolved iron in Svalbard fjords. The diagenetic reduction of glacially derived Fe oxides and the subsequent release of dissolved iron into pore waters may enhance 410 411 the *in-situ* formation of authigenic minerals in near-surface sediments, e.g., monosulphides and siderite (Görlich, 1986). This process is revealed by the high dissolved Fe concentrations (up to 800 412 µM) determined in porewaters in Kongsfjorden and Van Keulenfjorden (Wehrmann et al., 2014) and 413 other evidence for intense early diagenetic Fe reductions in other Svalbard fjords (e.g., Hornsund, 414 415 Tempelfjorden and Van Mijenfjorden; Vandieken et al., 2006 and references therein). The reduction of 416 Fe oxide releases abundant REEs. Therefore, the high export fluxes of dissolved Fe to Svalbard fjords 417 are also accompanied by the delivery of substantial amounts of dissolved REEs.

418

419 *5.2.2.* Seawater signals

One seawater ϵ_{Nd} data point is available from North Svalbard Sta#2 ($\epsilon_{Nd} \sim -11.8 \pm 0.4$ from 420 Andersson et al., 2008; 78.834°N, 9.330°E, ~199 m water depth) located only approximately 22 km 421 422 north-north west from the core site HH17-1086 (top-core authigenic $\varepsilon_{Nd} \sim -11.4 \pm 0.3$), i.e., the 423 northernmost station of Wijdefjorden (Fig. 1). The two sites lie at water depths of 150 m and 322 m in 424 comparable water masses characterized by the same density. The ϵ_{Nd} values of seawater and 425 authigenic sediment at both sites are consistent within uncertainty, suggesting the authigenic ε_{Nd} as an 426 archive of seawater Nd isotopic signatures (not preformed Fe oxides). 427 The seawater signals recorded in the authigenic ε_{Nd} can also be evaluated by comparing the

results from two nearby sites in Hornsund; HH15-1472 and HH16-1230 (for locations see Table S2

429 and Fig. 3). These two sites are located less than 2.2 km from each other but are separated by a sill 430 and hence are affected by different water masses, namely, TAW (HH15-1472) and WCW (HH16-1230) (Promińska et al., 2017; Zajączkowski et al., 2010) (Fig. 3). The ambient bottom water masses 431 432 at both sites can be clearly distinguished by different summer season temperatures, which are approximately 1°C in the outer fjord basin (TAW) and below -1°C in the inner basin (WCW) 433 434 (Zajączkowski et al., 2010). The surface sediments collected at the two sites show the same detrital ε_{Nd} values and almost identical major elemental geochemical composition, such as K/Al, Ca/Al, Fe/Ca 435 436 and Mg/Al ratios (Supplementary Table S3). However, the samples display different authigenic ε_{Nd} values (-12.1 at site HH15-1472 and -9.6 at site HH16-1230). This observation further highlights that 437 438 the authigenic ε_{Nd} signal preserved in the surface fjord sediments in Svalbard could be derived, at least 439 to some extent, from local water masses.

The authigenic ε_{Nd} values of the surface sediments collected near glacier fronts in Hornsund 440 (i.e., sampling sites HH16-1230, HH15-1482, and HH15-1486) are much more radiogenic than those 441 442 of the regionally advected water mass within the Sørkapp Current, which is an extension of the ESC (-443 $11.6 < \varepsilon_{Nd} < -10.6$ from Laukert et al., 2017; station 13; 78.834°N, 9.330°E, ~199 m water depth) (Fig. 444 1), suggesting strong preservation of radiogenic terrestrial inputs near the sources. Strong terrestrial signals could be partly due to efficient flocculation and, thus, the capture of small particles (including 445 446 Fe oxides) and their rapid deposition in the proximal environment (Markussen et al., 2016). However, 447 limitations exist in the simple comparison of isotopic compositions. Due to the transformation of 448 water masses carried by ESC and mixing with Atlantic water masses within WSC on the continental 449 shelf of western Spitsbergen, the water masses entering Hornsund fjord are a mixture of various water 450 masses (e.g., Promińska et al., 2017). Therefore, we cannot rule out the influence of seawater inflow 451 on the radiogenic authigenic ε_{Nd} .

452

453 5.3. Variation in the degree of Nd isotopic decoupling linked to climate-driven glacial system
454 changes

455 In Svalbard fjords, the authigenic ε_{Nd} values measured in surface sediments are

456 systematically more radiogenic than the corresponding detrital ε_{Nd} signatures. Consistent with

- 457 previous experimental investigations (see *section 5.1*), this observation further suggests that the
- 458 preferential release of radiogenic Nd occurs during weathering in a glacial environment.

459 Similar observations can be drawn from the downcore records acquired from Dicksonfjorden (site HH16-1202; Supplementary Table S4) and Woodfjorden (site HH12-964; Supplementary Table 460 461 S5), where the authigenic ε_{Nd} values are typically more radiogenic than the detrital ε_{Nd} values (Figs. 5 & 6). Interestingly, the differences between the authigenic and detrital values ($\Delta \varepsilon_{Nd}$) at these two sites 462 463 display similar variability over time (Fig. 7). Neodymium isotopic decoupling was enhanced (i.e., 464 leading to more positive $\Delta \epsilon_{Nd}$ values) since the mid-Holocene, when new glaciers formed (Fjeldskaar et al., 2018; Svendsen and Mangerud, 1997; van der Bilt et al., 2015) (growth curve of valley glacier 465 466 in Fig. 7) and/or existing glaciers on Svalbard readvanced ~4.5 ka (Baeten et al., 2010; Forwick et al., 2010) (growth curve of ice cap in Fig. 7). Decoupling is even more markedly enhanced during the 467 468 transition period and main phase of LIA, when most glaciers on Svalbard reached their maximum extent (e.g., Martín-Moreno et al., 2017; Svendsen and Mangerud, 1997) (Fig. 7). 469

470 Based on the above discussion (section 5.2), the observed strong decoupling between 471 authigenic and detrital signatures during the colder periods could indicate increasing contribution from (1) less radiogenic detrital materials, (2) inflow of radiogenic seawater and/or (3) more labile 472 473 terrestrial sources in the glaciated catchments. The first hypothesis, although it could partly explain 474 maximum $\Delta \epsilon_{Nd}$ values at the onset of and during parts of the LIA (Figs 5, 6, and 7) when decreased 475 ε_{Nd} of detrital fractions were documented, cannot account for the significant change in the $\Delta \varepsilon_{Nd}$ value 476 during the period of glacier growth at ~4.5 ka. Unfortunately, the very high diversity of rock types on 477 Svalbard combined with the sparse dataset on the measured ε_{Nd} in rocks (Table 1) limits the ability to 478 provide an exact explanation (sediment sources) for the observed temporal variability of ε_{Nd} in the 479 studied sediment cores. The second hypothesis concerning the enhanced inflow of advected seawater 480 likely cannot explain the observed changes, at least in Dicksonfjorden because of a shallow (~20 m) 481 sill at the fjord mouth, which has become slightly shallower in response to an isostatic rebound during 482 the mid-Holocene (Forman et al., 2004), thereby further restricting the inflow of external water

| 483 | masses. The third hypothesis concerning the increased input of labile terrestrial materials seems to |
|-----|---|
| 484 | provide a good explanation of the changes, particularly those recorded in Dicksonfjorden, where the |
| 485 | increased sediment accumulation rate ~4.5 ka (Fig. 5) indicates enhanced terrestrial inputs related to |
| 486 | the glacio-fluvial processes at that time. The glacial activity in Dicksonfjorden likely increased at |
| 487 | approximately 4.5 ka. This timing is synchronous with the glacier reformation in the catchment areas |
| 488 | of Linnévatnet (5 - 4 ka from Svendsen and Mangerud, 1997) and Hajeren lakes (~4.3 and ~3.3 ka |
| 489 | from van der Bilt et al., 2015) (Fig. 7). It also corresponded to the periods when Nordenskiöldbreen in |
| 490 | Billefjorden (5.5 - 3.2 ka from Baeten et al., 2010) and Tunabreen in Tempelfjorden (6 - 4 ka from |
| 491 | Forwick et al., 2010) grew (Fig. 7). Based on the evidence above, we propose that the downcore |
| 492 | fluctuations in $\Delta \epsilon_{Nd}$ in Svalbard fjord sediments, mainly at ~4.5 ka when several catchments were |
| 493 | likely re-occupied by glaciers, reflected changes in the degree of ϵ_{Nd} decoupling related to the |
| 494 | presence/growth (or absence/retreat) of adjacent glaciers and associated weathering conditions. We |
| 495 | hypothesize that the growth of glaciers provided freshly eroded rock substrates available for |
| 496 | subglacial weathering, thereby leading to the preferential release of radiogenic Nd (e.g., Süfke et al., |
| 497 | 2019) and ultimately more pronounced isotopic decoupling between authigenic and detrital ϵ_{Nd} values |
| 498 | in the fjord sediments (Fig. 7). An increase in the $\Delta \epsilon_{Nd}$ value at site HH12-964 in mid-Woodfjorden at |
| 499 | approximately 4.5 ka may also be attributed to the growth of tidewater glaciers draining into the |
| 500 | Woodfjorden system (Fig. 7), which is supported by an abrupt increase in the sand content at that time |
| 501 | (from less than 2 to 4.4 %; Hansen, 2014). We ruled out the potential influence of preformed Fe |
| 502 | oxides based on the discussion in section 5.2. However, the presence of preformed phases within |
| 503 | sediment that survived weak chemical weathering during the periods of glacier advances might partly |
| 504 | intensify $\Delta \varepsilon_{Nd}$ by increasing the authigenic ε_{Nd} . |
| EOE | Our finding that A group with ility in Saulhand find and incents many selfect week wing induced |

505 Our finding that $\Delta \epsilon_{Nd}$ variability in Svalbard fjord sediments may reflect weathering-induced 506 changes in Nd isotopic decoupling related to glacier cover has far-reaching implications. For instance, 507 $\Delta \epsilon_{Nd}$ could be used in future studies to reconstruct the impact of past glacial meltwater on marine 508 productivity (e.g., Wadham et al., 2019) as a proxy to infer historical glacial releases of key nutrients 509 (e.g., P and Fe) associated with the dissolution of accessory phosphate minerals and nano-particulate 510 iron oxides.

511

512 6. Conclusion

513 Our survey of Nd isotopes in leached and residual (detrital) components of Svalbard bedrock and ford sediment samples confirms that weathering under glacial conditions is accompanied by 514 515 incongruent weathering leading to significant Nd isotope decoupling. In Arctic environments, such as 516 Svalbard, glacier melting provides substantial amounts of nanoparticulate Fe oxides and dissolved 517 elements, resulting in abundant co-precipitation of hydrogenous Fe-oxyhydroxide phases in the nearby seawater/fjord environments and controlling, to a large extent, the distribution of leached 518 519 authigenic ε_{Nd} values in fjord sediments. The difference between authigenic and detrital ε_{Nd} values 520 (termed $\Delta \epsilon_{Nd}$) in the Holocene sedimentary records from the two fjords, Dicksonfjorden and 521 Woodfjorden show trends that mimic the evolution of glacier activity over the last millennia, related 522 to climate variability. The $\Delta \varepsilon_{Nd}$ values and inferred Nd isotopic decoupling were higher during the periods of glacier advances, e.g., at ~4.5 ka and during the LIA, suggesting that increased glacier 523 524 cover and concomitant glacial abrasion of fresh rock substrates resulted in intensified incongruent 525 chemical weathering. This novel Nd isotope approach ($\Delta \varepsilon_{Nd}$) may be used in future studies as a new 526 proxy for past glacial changes and associated glacial-derived nutrient inputs to the marine realm.

527

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538 References

- Andersson, P.S., Dahlqvist, R., Ingri, J., Gustafsson, Ö., 2001. The isotopic composition of Nd in a
- 540 boreal river: a reflection of selective weathering and colloidal transport. Geochim. Cosmochim. Acta
- 541 65, 521**-**527.
- 542 Andersson, P.S., Porcelli, D., Frank, M., Björk, G., Dahlqvist, R., Gustafsson, Ö., 2008. Neodymium
- isotopes in seawater from the Barents Sea and Fram Strait Arctic–Atlantic gateways. Geochim.
 Cosmochim. Acta 72, 2854-2867.
- 545 Baeten, N.J., Forwick, M., Vogt, C., Vorren, T.O., 2010. Late Weichselian and Holocene sedimentary
- environments and glacial activity in Billefjorden, Svalbard. Geol. Soc. Lond., Spec. Publ. 344, 207-223.
- 547 Bayon, G., Barrat, J.A., Etoubleau, J., Benoit, M., Bollinger, C., Révillon, S., 2009. Determination of
- rare earth elements, Sc, Y, Zr, Ba, Hf and Th in geological samples by ICP-MS after Tm addition and
- alkaline fusion. Geostand. Geoanal. Res. 33, 51-62.
- Bayon, G., German, C.R., Boella, R.M., Milton, J.A., Taylor, R.N., Nesbitt, R.W., 2002. An improved
 method for extracting marine sediment fractions and its application to Sr and Nd isotopic analysis.
- 552 Chem. Geol. 187, 179-199.
- Bayon, G., German, C.R., Burton, K.W., Nesbitt, R.W., Rogers, N., 2004. Sedimentary Fe-Mn
 oxyhydroxides as paleoceanographic archives and the role of aeolian flux in regulating oceanic
 dissolved REE. Earth Planet. Sci. Lett. 224, 477-492.
- Bayon, G., Vigier, N., Burton, K.W., Brenot, A., Carignan, J., Etoubleau, J., Chu, N.-C., 2006. The
- 557 control of weathering processes on riverine and seawater hafnium isotope ratios. Geology 34, 433-436.
- 558 Cottier, F., Tverberg, V., Inall, M., Svendsen, H., Nilsen, F., Griffiths, C., 2005. Water mass modification
- in an Arctic fjord through cross-shelf exchange: The seasonal hydrography of Kongsfjorden, Svalbard.
- 560 J. Geophys. Res. Oceans 110.
- 561 Dallmann, W., Elvevold, S., 2015. Bedrock Geology. Geoscience Atlas of Svalbard, Norsk Polarinstitutt,
- 562 Tromsø, Report Series 148, 133-173.
- 563 Dausmann, V., Gutjahr, M., Frank, M., Kouzmanov, K., Schaltegger, U., 2019. Experimental evidence

- for mineral-controlled release of radiogenic Nd, Hf and Pb isotopes from granitic rocks during
 progressive chemical weathering. Chem. Geol. 507, 64-84.
- 566 Elmore, A., Piotrowski, A., Wright, J., Scrivner, A., 2011. Testing the extraction of past seawater Nd
- 567 isotopic composition from North Atlantic deep sea sediments and foraminifera. Geochem. Geophys.
- 568 Geosyst. 12, Q09008, https://doi .org /10 .1029 /2011GC003741.
- Fjeldskaar, W., Bondevik, S., Amantov, A., 2018. Glaciers on Svalbard survived the Holocene thermal
 optimum. Quat. Sci. Rev. 199, 18-29.
- 571 Forman, S., Lubinski, D., Ingólfsson, Ó., Zeeberg, J., Snyder, J., Siegert, M., Matishov, G., 2004. A
- 572 review of postglacial emergence on Svalbard, Franz Josef Land and Novaya Zemlya, northern Eurasia.
- 573 Quat. Sci. Rev. 23, 1391-1434.
- Forwick, M., Vorren, T.O., 2009. Late Weichselian and Holocene sedimentary environments and ice
 rafting in Isfjorden, Spitsbergen. Palaeogeogr. Palaeoclimatol. Palaeoecol. 280, 258-274.
- 576 Forwick, M., Vorren, T.O., Hald, M., Korsun, S., Roh, Y., Vogt, C., Yoo, K.-C., 2010. Spatial and 577 temporal influence of glaciers and rivers on the sedimentary environment in Sassenfjorden and
- 578 Tempelfjorden, Spitsbergen. Geol. Soc. Lond., Spec. Publ. 344, 163-193.
- 579 Goldstein, S.J., Jacobsen, S.B., 1987. The Nd and Sr isotopic systematics of river-water dissolved 580 material: Implications for the sources of Nd and Sr in seawater. Chem. Geol. 66, 245-272.
- Görlich, K., 1986. Glacimarine sedimentation of muds in Hornsund fjord, Spitsbergen. Ann. Soc. Geol.
 Pol. 56, 433-477.
- 583 Gutjahr, M., Frank, M., Halliday, A.N., Keigwin, L.D., 2009. Retreat of the Laurentide ice sheet tracked
- by the isotopic composition of Pb in western North Atlantic seawater during termination 1. Earth Planet.
- 585 Sci. Lett. 286, 546-555.
- 586 Gutjahr, M., Frank, M., Stirling, C.H., Klemm, V., van de Flierdt, T., Halliday, A.N., 2007. Reliable
- 587 extraction of a deepwater trace metal isotope signal from Fe-Mn oxyhydroxide coatings of marine
- 588 sediments. Chem. Geol. 242, 351-370.
- 589 Hansen, T., 2014. Late Weichselian and Holocene sedimentary processes and glacier dynamics in
- 590 Woodfjorden, Bockfjorden and Liefdefjorden, North Spitsbergen. The Arctic University of Norway.

- Hawkings, J., Wadham, J., Tranter, M., Lawson, E., Sole, A., Cowton, T., Tedstone, A., Bartholomew,
- 592 I., Nienow, P., Chandler, D., 2015. The effect of warming climate on nutrient and solute export from the
- 593 Greenland Ice Sheet. Geochem. Perspect. Lett 1, 94-104.
- Hindshaw, R.S., Aciego, S.M., Piotrowski, A.M., Tipper, E.T., 2018a. Decoupling of dissolved and
- bedrock neodymium isotopes during sedimentary cycling. Geochem. Perspect. Lett. 8, 43-46.
- 596 Hindshaw, R.S., Tosca, N.J., Piotrowski, A.M., Tipper, E.T., 2018b. Clay mineralogy, strontium and
- neodymium isotope ratios in the sediments of two High Arctic catchments (Svalbard). Earth Surf.Dynam. 6, 141-161.
- Jacobsen, S.B., Wasserburg, G.J., 1980. Sm-Nd isotopic evolution of chondrites. Earth Planet. Sci. Lett.
 50, 139-155.
- Jang, K., Huh, Y., Han, Y., 2017. Authigenic Nd isotope record of North Pacific Intermediate Water
 formation and boundary exchange on the Bering Slope. Quat. Sci. Rev. 156, 150-163.
- Johansson, Å., Gee, D., Björklund, L., Witt-Nilsson, P., 1995. Isotope studies of granitoids from the
 Bangenhuk formation, Ny Friesland Caledonides, Svalbard. Geol. Mag. 132, 303-320.
- Joo, Y.J., Forwick, M., Park, K., Joe, Y., Son, Y.J., Nam, S.-I., 2019. Holocene environmental changes
- in Dicksonfjorden, west Spitsbergen, Svalbard. Polar Res. 38, 3426, https://doi .org /10 .33265
 /polar.v38 .3426.
- Kim, K., Choi, W., Hoffmann, M.R., Yoon, H.-I., Park, B.-K., 2010. Photoreductive dissolution of iron
 oxides trapped in ice and its environmental implications. Environ. Sci. Technol. 44, 4142-4148.
- 610 Laukert, G., Frank, M., Bauch, D., Hathorne, E.C., Rabe, B., von Appen, W.-J., Wegner, C., Zieringer,
- 611 M., Kassens, H., 2017. Ocean circulation and freshwater pathways in the Arctic Mediterranean based
- on a combined Nd isotope, REE and oxygen isotope section across Fram Strait. Geochim. Cosmochim.
 Acta 202, 285-309.
- Markussen, T.N., Elberling, B., Winter, C., Andersen, T.J., 2016. Flocculated meltwater particles
 control Arctic land-sea fluxes of labile iron. Sci. Rep.-UK 6, 24033, https://doi .org /10 .1038
 /srep24033.
- 617 Martín-Moreno, R., Allende Álvarez, F., Hagen, J.O., 2017. 'Little Ice Age' glacier extent and

- 618 subsequent retreat in Svalbard archipelago. The Holocene 27, 1379-1390.
- Moore, R., Burton, J., Williams, P.L., Young, M., 1979. The behaviour of dissolved organic material,
 iron and manganese in estuarine mixing. Geochim. Cosmochim. Acta 43, 919-926.
- 621 Pin, C., Zalduegui, J.S., 1997. Sequential separation of light rare-earth elements, thorium and uranium
- by miniaturized extraction chromatography: Application to isotopic analyses of silicate rocks. Anal.
- 623 Chim. Acta 339, 79-89.
- Poulton, S.W., Raiswell, R., 2005. Chemical and physical characteristics of iron oxides in riverine and
 glacial meltwater sediments. Chem. Geol. 218, 203-221.
- 626 Promińska, A., Cisek, M., Walczowski, W., 2017. Kongsfjorden and Hornsund hydrography -
- 627 comparative study based on a multiyear survey in fjords of west Spitsbergen. Oceanologia 59, 397-412.
- 628 Raczek, I., Jochum, K.P., Hofmann, A.W., 2003. Neodymium and strontium isotope data for USGS
- 629 reference materials BCR-1, BCR-2, BHVO-1, BHVO-2, AGV-1, AGV-2, GSP-1, GSP-2 and eight
- 630 MPI-DING reference glasses. Geostandard. Newslett. 27, 173-179.
- Rasmussen, T.L., Forwick, M., Mackensen, A., 2012. Reconstruction of inflow of Atlantic Water to
- Isfjorden, Svalbard during the Holocene: Correlation to climate and seasonality. Mar. Micropaleontol.94, 80-90.
- Rutberg, R.L., Hemming, S.R., Goldstein, S.L., 2000. Reduced North Atlantic Deep Water flux to the
- 635 glacial Southern Ocean inferred from neodymium isotope ratios. Nature 405, 935-938.
- 636 Süfke, F., Gutjahr, M., Gilli, A., Anselmetti, F.S., Glur, L., Eisenhauer, A., 2019. Early stage weathering
- systematics of Pb and Nd isotopes derived from a high-Alpine Holocene lake sediment record. Chem.Geol. 507, 42-53.
- Svendsen, J.I., Mangerud, J., 1997. Holocene glacial and climatic variations on Spitsbergen, Svalbard.
 The Holocene 7, 45-57.
- 641 Tanaka, T., Togashi, S., Kamioka, H., Amakawa, H., Kagami, H., Hamamoto, T., Yuhara, M., Orihashi,
- 642 Y., Yoneda, S., Shimizu, H., Kunimaru, T., Takahashi, K., Yanagi, T., Nakano, T., Fujimaki, H., Shinjo,
- 643 R., Asahara, Y., Tanimizu, M., Dragusanu, C., 2000. JNdi-1: a neodymium isotopic reference in
- 644 consistency with LaJolla neodymium. Chem. Geol. 168, 279-281.

- Taylor, P.C., Cai, M., Hu, A., Meehl, J., Washington, W., Zhang, G.J., 2013. A decomposition of
 feedback contributions to polar warming amplification. J. Climate 26, 7023-7043.
- 647 van der Bilt, W.G.M., Bakke, J., Vasskog, K., D'Andrea, W.J., Bradley, R.S., Ólafsdóttir, S., 2015.
- 648 Reconstruction of glacier variability from lake sediments reveals dynamic Holocene climate in Svalbard.
- 649 Quat. Sci. Rev. 126, 201-218.
- Vance, D., Teagle, D.A., Foster, G.L., 2009. Variable Quaternary chemical weathering fluxes and
 imbalances in marine geochemical budgets. Nature 458, 493-496.
- Vandieken, V., Finke, N., Jørgensen, B.B., 2006. Pathways of carbon oxidation in an Arctic fjord
- 653 sediment (Svalbard) and isolation of psychrophilic and psychrotolerant Fe(III)-reducing bacteria. Mar.
- 654 Ecol. Prog. Ser. 322, 29-41.
- von Blanckenburg, F., Nägler, T.F., 2001. Weathering versus circulation-controlled changes in
 radiogenic isotope tracer composition of the Labrador Sea and North Atlantic Deep Water.
 Paleoceanography 16, 424-434.
- 658 Wadham, J.L., Hawkings, J.R., Tarasov, L., Gregoire, L.J., Spencer, R.G.M., Gutjahr, M., Ridgwell, A.,
- Kohfeld, K.E., 2019. Ice sheets matter for the global carbon cycle. Nat. Commun. 10, 3567.
- 660 Wehrmann, L.M., Formolo, M.J., Owens, J.D., Raiswell, R., Ferdelman, T.G., Riedinger, N., Lyons,
- 661 T.W., 2014. Iron and manganese speciation and cycling in glacially influenced high-latitude fjord
- 662 sediments (West Spitsbergen, Svalbard): Evidence for a benthic recycling-transport mechanism.
- 663 Geochim. Cosmochim. Acta 141, 628-655.
- 664 Werner, K., Frank, M., Teschner, C., Müller, J., Spielhagen, R.F., 2014. Neoglacial change in deep water
- exchange and increase of sea-ice transport through eastern Fram Strait: evidence from radiogenic
- 666 isotopes. Quat. Sci. Rev. 92, 190-207.
- 667 Zajączkowski, M., Szczuciński, W., Plessen, B., Jernas, P., 2010. Benthic foraminifera in Hornsund,
- 668 Svalbard: Implications for paleoenvironmental reconstructions. Pol. Polar Res. 31, 349-375.
- 669









683 Figure 2. (A) Map of Svalbard showing the sampling locations (B) to (F) for the bedrock. The ε_{Nd} 684 values of detrital and weatherable components in the catchment areas of Woodfjorden (B), Kongsfjorden (C) and Isfjorden and its tributary Billefjorden (D, E, and F) are marked with 685 686 green rectangles. Samples with too little Nd to obtain data are marked with an 'x'. ε_{Nd} values 687 with high uncertainties (> 0.5 epsilon-unit) are in red numbers. The bedrock samples include 688 sixteen sedimentary rocks and two metamorphic rocks. Various bedrock ages are marked with 689 different symbols. For comparison, the ε_{Nd} value measured from whole rocks in Ny-Friesland 690 (for location see Fig. 1) is also marked with pink ellipses in Fig 2A (data from Johansson et al., 691 1995). The geologic map is modified after Dallmann and Elvevold (2015).



Figure 3. Maps of the locations of fjord sediments (left column). ε_{Nd} of detrital (central column) and authigenic (right column) components within surface sediments collected from (A) Hornsund, (B) Dicksonfjorden, Isfjorden, Tempelfjorden, (C) Woodfjorden, Wijdefjorden, and (D) Van Mijenfjorden. The present glacier fronts in Hornsund (summer 2015) are indicated by blue dashed lines, and major sills in Hornsund and Dicksonfjorden are marked by red dotted lines.



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Figure 4. ε_{Nd} data comparison between leached (authigenic and weatherable) and residual components (detrital) of the bedrock samples (red squares), surface sediments (white diamonds), core sediments at sites HH12-964 (blue diamonds) and HH16-1202 (green diamonds). For further comparison, the ε_{Nd} values of the corresponding components within bedrocks and glacial sediments (yellow stars) and riverine dissolved and suspended loads (purple circles) in Svalbard, as well as seawater range at the Spitsbergen margin (green bar) are also shown (data from Andersson et al., 2008; Hindshaw et al., 2018a; Hindshaw et al., 2018b; Laukert et al., 2017).



712Figure 5. Temporal variation in ε_{Nd} values of detrital (red) and authigenic (blue) components at site713HH16-1202 in Dicksonfjorden. The ε_{Nd} data are compared to the IRD flux (black) and sediment714accumulation rate (dark pink) (Joo et al., 2019). Error bars for ε_{Nd} represent $\pm 2\sigma$ uncertainties.



717Figure 6. Temporal variation in ε_{Nd} values of detrital (red) and authigenic (blue) components at site718HH12-964 in Woodfjorden. The ε_{Nd} data are compared to the sediment accumulation rate719(Hansen, 2014). Error bars for ε_{Nd} represent $\pm 2\sigma$ uncertainties.





723Figure 7. Comparison of (A) the differences between the authigenic and detrital ε_{Nd} values ($\Delta \varepsilon_{Nd}$) at724core sites HH12-964 (red) and HH16-1202 (blue) and (B) the glacier thickness reconstructed by725the best-fit model after Fjeldskaar et al. (2018) over the last 8 ka. Higher $\Delta \varepsilon_{Nd}$ values typically726occur during the periods of glacier advances (green bars). Error ranges for $\Delta \varepsilon_{Nd}$ were calculated727based on a smoothing spline Monte-Carlo simulation (2σ , resampled at every 0.1 ka, n =728100,000).

| Sample ID | Coordinate | Area | Stratigraphic unit | Age* | Rock type | Detrital ENd | Weatherable _{ENd} |
|-----------------|-----------------------|---|--|--|----------------------|-----------------------|-------------------------------|
| 13071104 | 78.987°N, 12.087°E | Blomstrandhalvøya, Kongsfjorden | Generalfjella Formation (Fm.), Krossfjorden Group | Upper Proterozoic | Quartzite | -8.8 ± 0.2 | -5.8 ± 0.2 |
| 13071105 | 78.987°N, 12.087°E | Blomstrandhalvøya, Kongsfjorden | Generalfjella Fm., Krossfjorden Group | Upper Proterozoic | Phyllite | -11.7 ± 0.3 | -11.4 ± 0.4 |
| SK01 | 78.545°N, 16.183°E | Skansen, Isfjorden- Billefjorden | Wood Bay Fm., Dicksonfjorden Member | Devonian | Sandstone | $\textbf{-8.6}\pm0.3$ | -6.4 ± 0.3 |
| 080302 | 79.389°N, 13.622°E | Halvdanpiggen, Woodfjorden | Wood Bay Fm. | Devonian | Red sandstone | -13.6 ± 0.3 | $\textbf{-10.8}\pm0.2$ |
| 13071005 | 78.953°N, 11.758°E | Brøggerhalvøya, Kongsfjorden | Brøggertinden Fm. | Carboniferous | Red sandstone | -3.6 ± 1.3 | -12.6 ± 0.2 |
| SYB05 | 78.944°N, 11.724°E | Brøggerhalvøya, Kongsfjorden | Wordiekammen Fm. | Carboniferous | Limestone | - | - |
| SYB56 | 78.941°N, 11.703°E | Brøggerhalvøya, Kongsfjorden | Wordiekammen Fm. | Carboniferous | Dolostone | - | $\textbf{-10.9}\pm0.6$ |
| SK20 | 78.539°N, 16.159°E | Skansen, Isfjorden- Billefjorden | Wordiekammen Fm. | Carboniferous | Dolostone | - | - |
| SYB40.1 | 78.942°N, 11.704°E | Brøggerhalvøya, Kongsfjorden | Wordiekammen Fm. | Carboniferous - Permian | Calcareous shale | -16.3 ± 0.3 | -13.7 ± 0.3 |
| SF00.5 | 78.915°N, 11.654°E | Brøggerhalvøya, Kongsfjorden | Kapp Starotin Fm. | Permian | Chert | -11.6 ± 0.5 | -6.6 ± 0.2 |
| 080109 | 78.091°N, 13.81°E | Festningen, Isfjorden- Grønfjorden | Kapp Starotin Fm. | Permian | Black mudstone | -8.5 ± 0.3 | -6.8 ± 0.2 |
| Sval central | 78.545°N, 16.183°E | Skansen, Isfjorden- Billefjorden | Kapp Starotin Fm. | Permian | Anhydrite | - | - |
| KIGAM #25 | 78.475°N, 15.812°E | Rotundafjellet, Isfjorden- Billefjorden | Sassendalen Group | Early – Mid. Triassic | Shale | $\textbf{-6.1}\pm0.4$ | -9.3 ± 0.2 |
| 080111 | 78.094°N, 13.837°E | Festningen, Isfjorden- Grønfjorden | Verdebukta Fm. | Triassic | Black mudstone | -10.6 ± 0.3 | -8.7 ± 0.2 |
| 20150901- 02 | 78.341°N, 15.857°E | Janusfjellet, Isfjorden- Adventfjorden | Marhøgda Bed, Agardhfjellet Fm. | Jurassic | Oolitic ironstone | $\textbf{-6.3}\pm0.3$ | -5.1 ± 0.3 |
| KIGAM #16 | 78.098°N, 13.913°E | Festningen, Isfjorden- Grønfjorden | Janusfjellet Subgroup | Mid. Jurassic - Early Cretaceous | Shale | 3.4 ± 0.4 | -1.2 ± 0.3 |
| KIGAM #5 | 78.239°N, 15.337°E | Platåberget, Isfjorden- Adventfjorden | Carolinefjellet Fm. | Early Cretaceous | Shale | -9.0 ± 0.2 | -12.0 ± 0.2 |
| 080114 | 78.099°N, 13.948°E | Festningen, Isfjorden- Grønfjorden | Helvetiafjellet Fm. | Cretaceous | Sandstone | -25.9 ± 0.2 | -25.6 ± 0.2 |
| *Dollmor | n and Elva | $\frac{1}{12}$ | | | | | |

730 Table 1. Detrital and weatherable ϵ_{Nd} values of Svalbard bedrocks.

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*Dallmann and Elvevold (2015)