

Interactive comment on “Trace elements and cathodoluminescence of detrital quartz in Arctic marine sediments – a new ice-rafted debris provenance proxy” by A. Müller and J. Knies

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Reply to discussion: Müller and Knies CPD 9, 4145-4189: “Trace element and cathodoluminescence . . . ice-rafted debris provenance proxy”

In general, we appreciated the constructive comments of both reviewers and changed the manuscript accordingly. Our replies to the specific reviewer comments are as follows:

Reviewer #1

Reviewer comment: “In terms of my own “expertise” I would claim both an interest and

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knowledge of ice-rafting processes, but I have had very little to no experience in the tracers used in this study. One small point before I discuss some major issues—my colleague at the University of Colorado is Lang Farmer, i.e. his 1st name is Lang (see references—they should be Farmer, L.). I certainly support the publication of this paper as it has the potential to address a critical issue in many IRD studies, and that is trying to better identify source(s) for that the ubiquitous mineral—quartz. Because this is all about quartz then I suggest they should reference Kolla, V., Biscaye, P.E., Hanley, A.F., 1979. Distribution of quartz in Late Quaternary sediments in relation to climate. *Quaternary Research* 11, 261-277 and also Bond’s efforts to identify source(s) based on the hematite stains on sand-size quartz grains. Nevertheless, their assertion that characterizing the provenance of quartz in Quaternary sediments is an important objective for IRD studies is totally correct.”

Reply: We corrected the reference “Farmer et al.” and added the references.

Bond, G., Showers, W., Cheseby, M., Lotti, R., Almasi, P., deMenocal, P., Priore, P., Cullen, H., Hajdas, I., Bonani, G. 1997. A pervasive millennial-scale cycle in North Atlantic Holocene and glacial climates. *Science*, 278, 1257-1266.

Bond, G., Kromer, B., Beer, J., Muscheler, R., Evans, M.N., Showers, W., Hoffmann, S., Lotti-Bond, R., Hajdas, I., Bonani, G. 2001. Persistent solar influence on north Atlantic climate during the Holocene. *Science*, 294, 2130-2136.

Reviewer comment: “I think the authors might say a little at the beginning about the grain-size spectra of their sediments. I think many researchers have the mistaken belief that when “we” talk about IRD that the sediments contain a great wt% of coarse sand. In my experience this is not the case and even in this study it appears that quartz grains were not all that plentiful. What was the fraction of quartz versus other minerals in this size range?”

Reply: An additional paragraph was added at the end of chapter 3.1: “The grain-size spectra in Setting B samples consist of sand-bearing clayey silts, with sand contents

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varying between 0 and 6 wt. % (Winkelmann, 2003). The sand content in Setting A samples of Setting A may reach up to 30 wt.% of the total fraction. In the >500 μm fraction, the fraction of quartz relative to other minerals was between 10 and 20 %."

Winkelmann, D., 2003. Reconstruction of recent and late Holocene sedimentation processes on the continental shelf west off Spitsbergen, Diploma Thesis, Freiberg University of Mining and Technology. pp. 156.

As an example for the grain size spectra of setting B, the grain size distribution for three stations in the Storfjorden, southern Spitsbergen, is shown in Figure 1.

Reviewer comment: "However, when considering any laboratory method and its research application there are two vital issues that need to be discussed "up front" (at least in my mind) – they are the time taken to process samples, and then what is the cost. I do not think more than a paragraph is needed but with a new method then I suggest that these are important questions. For example, how long did it take to garner the 198 quartz grains etc etc. These issues become critical if someone was thinking of using this method in order to obtain multi-decadal records over a 1-2 cal ka interval. This is where the potential costs will also come in—what would be the cost for example of processing say 100 samples?"

Reply: An additional paragraph was added at the end of chapter 1: "Processing and analyzing the offshore (9) and onshore (18) samples with our new quantitative approach are relatively fast. For the LA-ICP-MS analyses (133 offshore quartz grains; 53 quartz grains in onshore samples), we used 20 working days including data processing. Initial handpicking of 198 quartz grains, preparation of thick sections, investigations by optical microscopy and SEM and SEM-CL work lasted another ca. 30 working days. The analysis of ca. 100 samples to obtain information on the origin of IRD-derived quartz grains in a millennial-centennial record outside Svalbard will last ca. 7 months with this new approach."

A general comment to the raised questions above: The handpicking of 198 grains

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out from the 500 μm took about two days. After hand picking the sand grains were embedded in epoxy resin and polished down half size as we described in our paper. The mounting of the sand grains was carried out at the thin section laboratory at the Geological Survey of Norway (NGU). 18 petrological polished thick (~300 μm) sections were prepared from the onshore samples. The sample preparation took two months and the cost per mount was ca. 64 Euro (25 mounts and 18 sections were prepared with a total cost of 2752 Euro). Five working days were spent for optical microscopy and 20 working days for SEM and SEM-CL investigations at NGU. For the LA-ICP-MS analyses – 133 analyses of offshore quartz grains and 53 analyses on onshore samples - we used 20 working days including data processing. Summarizing we used about 2 months for the preparation and analyses of 9 offshore sand samples and 18 onshore hard rock samples. To answer your question: The preparation and analyses of 100 samples would require 7 months working time applying the preparation costs of NGU and the working efficiency of the authors.

The costs for applying the analytical methods are different for different laboratories and prices change with time. NGU has access to all facilities in its own laboratory, and costs are therefore rather moderate. Furthermore, people work in different ways and with different efficiency and, thus, the time needed will be different for different people. For that reasons, we cannot estimate the exact working time and costs for each individual project applying this approach, and we are not aware of any scientific paper in which prices and time estimation for sample preparation and analyses are provided.

Reviewer comment: Another major concern I had was with the identification of the quartz groups (p. 4152) i.e. "...offshore samples were classified into five major types..." It is not clear to me 1) how these groups were initially defined, and 2) are they indeed "unique", i.e. what is the probability of assigning a grain to only one group? The criteria for placing a quartz grain in one of the 5 groups, A to E, are complex and not necessarily numeric but when I look at the plots on Fig. 6 my first question is:

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how distinct are the designated groups? This could be tested by Discriminant Function Analysis (DFA) under the null hypothesis that there are no differences between the groups based on the element analysis. However, in Table 3 (p. 4169) the distinction between groups A, B and C re primary and secondary rock types appears marginal at best—or do I misunderstand?

Reply: We wrote in our paper: "The quartz grains of offshore samples were classified into five major types, A to E, based on mineral micro inclusions, CL intensity, intra-granular structures visualized by SEM-CL imaging and trace element content." which answers your point (1). This statement implies that classification was developed on the base of the observed, most significant features of the investigated offshore grains. Thus, the classification application is restricted to the offshore sample area of this study. In a number of onshore rock samples we found quartz grains with features which were not observed in offshore grains. For these grains a classification was not necessary because they could immediately be excluded as the source of offshore grains. We choose the features distinguishing the groups in that way that each offshore grain could assigned to one group only. With the applied classification we identified successfully the source area of most of the onshore grains and, therefore, the classification is distinctive enough for this study. To make us more clearly we did a number of changes at the beginning of the chapters 5.1 and 5.2.

Reviewer comment: "The authors demonstrate the power of the method in terms of a relatively small (i.e. small in the context of the NH ocean which would today or in the past be subject to IRD) region. The underlying question that I pose to them is this: does your characterization of the quartz grains carry enough information that we are likely (probably?) to be able to discriminate between quartz grains of similar origins (e.g. Table 3) from say NE Greenland versus SW Spitsbergen? They might legitimately answer that this is the next step, but...they probably know enough of the regional geology of these areas as to hazard a guess or a best case scenario because after-all, for this method to have widespread utility then it needs to be able to differentiate, if

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possible, between rocks of similar ages and origins (the Old Red Sandstone) but which are now disjunct. I am certainly not advocating that this needs to be done for this paper, but this is the larger and more important issue that this paper, and methods, raise. "

Reply: An additional paragraph was added to chapter 7: "The next steps will be (1) collecting and analysing further onshore samples from Svalbard to expand the database for further IRD provenance studies in this climate-sensitive region, and (2) start analysing down-core records from the Yermak Plateau, an area influenced by former paleo ice streams (e.g. Gebhardt, et al., 2011) and variable sea ice conditions (Fig. 2). On a longer term perspective, onshore samples from Greenland, Scandinavia and Iceland will be added to the database delineating major IRD provinces in the circum North Atlantic - Arctic Ocean further."

Gebhardt, A.C., Jokat, W., Niessen, F., Matthiessen, J., Geissler, W.H., and Schenke, H.W., 2011. Ice sheet grounding and iceberg plow marks on the northern and central Yermak Plateau revealed by geophysical data. *Quaternary Science Reviews*, v. 30, p. 1726-1738.

A general comment to the raised issue: The quartz grains of the studied area carry enough information to identify the source area. Taking our results in consideration: yes, it is probably possible to discriminate between quartz grains from NE Greenland and SW Spitsbergen, but we simply do not know, because - to our knowledge - there are no data of CL structures and trace element contents of quartz in onshore rocks from NE Greenland available. On a longer perspective, we need to build up this database for the circum Atlantic-Arctic IRD provinces to improve this knowledge. We currently have only a sufficient overview about potential quartz grains being derived from Svalbard and western Scandinavia.

Reviewer #2

Reviewer comment: "In the Introduction the authors refer to the review paper of Hemming (2004, focusing on Heinrich layers in the North Atlantic!) for outlining the impor-

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tance of IRD provenance studies. This statement is followed by a brief listing of other proxies mainly applied to central Arctic Ocean sediments. However, as this manuscript focuses on the western Svalbard margin, a bit more detailed review of the large number of studies (e.g., Elverhøi et al. 1995, Andersen et al. 1996, Hebbeln et al. 1994, papers by Jens Bischof and by the Tromsø group and others) dealing with IRD provenance from exactly this region definitely would improve the paper. It would be especially good to know, which proxies (lithology, mineralogy, clay minerals, but also those referred to in the above mentioned listing: Nd isotopes etc.) have been successfully applied and where we still have major gaps in tracking IRD provenance. Also sediment trap studies from the region have been used to link sea ice transported material to sea ice advection from eastern Svalbard by the East Spitsbergen Current (Berner & Wefer 1994, Hebbeln 2000).”

Reply: Yes, we agree and have added new references and re-structured the introduction completely. The new version of the introduction chapter is shown below: 1 Introduction Provenance studies of ice-rafted debris (IRD) in the North Atlantic – Barents Sea are a remarkable tool for providing insights into the dynamics of large ice-sheets and the timing and duration of their disintegration (e.g. Hemming, 2004 for a review). Prominent IRD layers in the North Atlantic – the sedimentological expression of ice-sheet surging during a Heinrich event - and their origins illustrate the complexity of ice-sheet – ocean interactions in the Northern Hemisphere during the last glacial period (e.g. Kolla et al., 1979; Grousset et al., 1993; Bond et al., 1997, 2001; Farmer et al., 2003; Peck et al., 2007; Andrews et al., 2009; Verplanck et al., 2009). Identifying the provenance of such IRD layers in the Arctic is, however, not straightforward because of the abundance of IRD from both sea ice and glacial rafting (Stein 2008, for review). For instance, the provenance of IRD-rich sediments along the Spitsbergen continental margin has been constrained by various approaches including bulk/clay mineralogy (Elverhøi et al., 1995; Andersen et al., 1996; Vogt et al., 2001; Forwick et al., 2010), petrography of dropstones (>500 μm) (Bischof, 1994; Hebbeln et al., 1994, 1998), iron grain chemical fingerprinting (Darby et al., 2002) and stable isotope geochemistry (Sr,

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Nd) (Tütken et al., 2002). The results of all studies have demonstrated their potential to provide insights into both the changing sea ice drift patterns in the Arctic Ocean and the complex Eurasian ice-sheet history during the Quaternary. The application of these provenance proxies is particularly relevant for identifying large scale geological provinces and thus circum-North Atlantic/Arctic ice sheet dynamics and sea ice patterns. However, they are limited to pin point the exact bedrock formation onshore and consequently delineating material derived through glacial erosion, transport, and deposition from individual ice stream (ice sheet) dynamics over time.

In the present study, we focus on detrital quartz grains in the >500 μm fraction of marine sediments offshore of Spitsbergen considered to be IRD derived from melting icebergs and sea ice (cf. Elverhøi et al., 1995; Hebbeln et al., 1998). Potential source rocks for specific bedrock formations are constrained by introducing a new analytical approach combining structural studies of quartz grains by optical microscopy, scanning electron microscope backscattered electron imaging (SEM-BSE), scanning electron microscope cathodoluminescence imaging (SEM-CL) with chemical analyses of quartz grains by laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS). Quartz is a mineral preferred for provenance studies due to its resistance to weathering and common presence in rocks and soils. The structural analysis of detrital quartz grains in sedimentary rocks by means of optical microscopy and SEM-CL has a long history in provenance evaluation in sedimentology (e.g. Seyedolali et al., 1997; Götze and Zimmerle, 2000 and references therein). Recent developments of micro beam techniques, such as LA-ICP-MS and secondary ion mass spectrometry enable the chemical characterisation of quartz grains down to $\sim 100 \mu\text{m}$ in size. Chemical analyses have shown that the trace element signature of quartz is controlled by the physicochemical conditions of quartz formation (e.g. Götze, 2009 and references therein) and, thus, represents a geochemical fingerprint of the quartz origin. However, the chemical characterisation of quartz grains by these analytical techniques has not been applied for provenance studies so far.

Up to now, we have studied 9 core-top (0-1 cm) samples randomly distributed along the western and southern coast of Spitsbergen (Fig. 1) and compared the quartz properties in the >500 μm fraction with 18 onshore samples from potential source areas in central, west, south and southeast Spitsbergen. Our results show that various bedrock provinces in the study area are identifiable in the quartz grains offshore of Spitsbergen. Long-distance transport by sea ice is the dominant transport mechanism for the quartz grains. In addition, quartz grains released from melting icebergs/sea ice, originating from either central or southeastern Spitsbergen, are clearly recognized. Considering the complicated glacial dynamics of former Barents Sea ice sheets as recently outlined by Dowdeswell et al. (2010), this new approach applied to Arctic continental margin sediments will help to define the sources of IRD and thus spatial/temporal changes in ice-flow drainage patterns better.

Reviewer comment: "Although I trust in their conclusion that most of the IRD comes from eastern Svalbard (as also other studies have shown before, see above), I am a bit skeptical regarding the reasoning. With their method the authors identify typical populations of the quartz types A-E related to specific onshore source areas. At the end they link these populations to those populations found in the sea floor samples. However, after uptake by sea ice and icebergs and after transport, the final deposition of the IRD will largely take place as individual grains. So, I wonder how the "artificial" population made up by these individual grains coming from a variety of icebergs/sea ice deposition events can be compared to populations being derived from a discrete rock sample? Maybe that works out, but to be convinced I would like to see some statistics."

Reply: First part of the reviewer comment: Our paper is structured in that way that we first classified the IRD quartz grains >500 μm found in offshore samples into five groups on the base of mineral micro inclusions, CL intensity, intra-granular structures visualized by SEM-CL imaging and trace element content. The classification was developed by means of the observed, most significant features of the investigated offshore grains

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and, thus, the classification application is restricted to the offshore sample area of this study. The distinguishing features were chosen in that way that each offshore grain could be assigned to one group only. We did not use properties of quartz of onshore samples for the classification. In the second step onshore quartz, where possible, was assigned to one of the grain type groups defined by the offshore samples. However, a number of onshore samples contain quartz grains with features which were not observed in offshore grains. For these grains a classification was not necessary because they could immediately be excluded as the source of offshore grains.

To make the establishment of our classification more clearly we added explaining sentences at the beginning of the chapters 5.1 and 5.2.

Second part of the comment: Almost all offshore regions sampled contain grains of the "artificial" groups A and B and these groups represent the major quartz-grain populations in the >500 μm size fraction. The onshore samples which were collected from possible provenance regions in the catchment areas of rivers and surging glaciers relative close to the offshore samples contain often (about 60% of the samples) A type grains. However, none of the onshore samples contain type B grains except the samples from the Late Triassic De Geerdalen Formation at Egdeøya. These B type grains are rather specific (compared to the almost featureless A type grains) being polycrystalline and polyphase quartz grains intergrown with K-feldspar, mica (biotite and/or muscovite), chlorite, and calcite and containing micro inclusions of apatite, pyrite, Fe oxides, calcite, dolomite, barite, rutile, zircon, and monazite. The grains originate (originally) from low-grade metamorphic quartzites which do not occur on Spitsbergen today. The remains of sericite and Fe-oxides/hydroxides on the grain surfaces indicate that they are detrital grains from eroded sandstones (secondary origin). The rocks of the De Geerdalen Formation cover more than 50% of the surface of Egdeøya and Barentsøya and almost 100% of the island Hopen which corresponds to more than 3000 km² (Fig. 1). (We added the previous sentence to the manuscript to underline the enormous extension of this stratigraphic unit.) Thus, the identified source rocks

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are not just locally outcropping rocks. The area of the inner Storfjord, Barentsøya and Egdeøya are the major iceberg-producing areas in southern Spitsbergen (Dowdeswell and Dowdeswell, 1997) and the icebergs and sea ice formed there are transported by the East Spitsbergen Current (ESC) from Storfjord westward around southern Spitsbergen continuing northward along the continental shelf, passing Forlandsund and Prins Karls Forland. Occasionally westerly winds blow drift ice coming with the ESC in the inner parts of the fjords along the western coast, namely Hornsund, Van Mijenfjord, Isfjord and Kongsfjord (Umbreit, 2009), implying that even the sample sites 1258 and 1265 might be affected by ESC drift ice. The grain-type distribution statistics in form of pie charts shown in Figure 5 illustrate impressively that the source of type B grains is with very high possibility the sandstones of the De Geerdalen Formation. However, our study represents a pilot study and in the frame of this study we were able to sample only a certain amount of onshore samples. We tried to cover all major sequences in the possible catchment areas which contain quartz grains $>500 \mu\text{m}$.

Reviewer comment: "If the high amount of Type D quartz in sample 1265 is indicative for a local source, where is the considerable amount of type B quartz in this sample coming from as it is not found in the surrounding onshore samples?"

Reply: Type D grains which represent the major grain population in the sample 1265 from the inner Isfjord are interpreted to originate from sandstones of the Kapp Toscana and Adventdalen Group. These units are in the catchment area of the tidewater glaciers of the Tempelfjord and - in historical times - Sassendal and are the major source of drift ice in inner Isfjord (cf. Forwick and Vorren, 2009). The second, minor source of drift ice in the Isfjord is the area of Storfjord from where ice is transported by the ESC around southern Spitsbergen and blown by common westerly winds into the inner parts of the Isfjord (Umbreit, 2009). Thus, type B grains in sample 1265, forming the minor population, are interpreted as IRD originating from the Triassic De Geerdalen Formation at Edgeøya, Barentsøya and inner Storfjord. We added the last two sentences to the manuscript.

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Reviewer comment: "The type E grains in sea floor sample 1244 are linked to the only onshore sample containing this type of grains: DH7A-1. However, according to Fig. 5 this sample is located close to the Isfjord, where this group of samples has been used to explain the high contribution of type D sediments to the Isfjord sample 1265 (see above). Maybe this is a matter of clear presentation in the figure. But as it is presented now, it is somewhat confusing."

Reply: Type E grains are rather specific comprising fine-grained arkose fragments (2 to 3 mm) containing predominantly detrital rounded quartz grains and some K-feldspar grains cemented by non-luminescent authigenic quartz. In the onshore samples this grain type was found only in the sandstone sample DH7A-1 of the Early Cretaceous Adventdalen Group from southern Isfjord. Exposures of the Adventdalen Group extend from north Adventdalen, south Isfjord, to Argadhaldalen at the western coast of Storfjord (Fig. 1). The location of sample 1244 is relatively close to surging glaciers north and south of Argadhaldalen whose catchment areas are partially in the Adventdalen sandstones. We changed the manuscript accordingly for clarification.

Reviewer comment: "Sample 1246 from the southern Storfjord that is right in the proposed main IRD transport path, contains quite some Type C grains that are not common in the proposed source area on Edgeøya. A comment on this observation would be great."

Reply: In chapter 5.1, where the type C grains are described we wrote "Coatings of sericite and Fe-oxides/hydroxides at the grain surfaces (see black arrow in Figure 4) indicate that type C grains represent detrital grains from eroded sandstones (secondary origin) similar to type A and B grains." Further on in the discussion chapter 6 we wrote: "However, it appears that types A, B and C grains are regionally and genetically connected." . . . and "Thus, the most likely regional sources of the IRD for type A, B, and C are the east coast of Edgeøya and Barentsøya and the inner Storfjord (Fig. 5)." We think, that this findings and explanations express clearly that type C grains belong to the assemblage of A and B type grains which originate from Egdeøya.

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Reviewer comment: Finally, the entire region has been glaciated several times with the last glaciation being just 20 ka ago. Glacial erosion and transport probably have distributed quartz grains from various source regions to all around the north-eastern Barents Sea. And, of course, also these glacial sediments can be picked up by icefloes and icebergs probably delivering a quite variable quartz signal to the western Svalbard margin. In which way would such a “reworked source” signal interfere with the conclusions drawn in the manuscript?

Reply: This is exactly the beauty of this new approach! By studying a LGM-deglaciation-Holocene record from the western Svalbard margin (or any other margin where we have control on the sources for the detrital quartz), we identify first the exact bedrock formation that sourced the detrital quartz grains in the marine record during a specific time interval. Second, we then reconstruct the controlling processes for erosion/transport of detrital quartz for each (crucial) time interval. For instance, during the LGM we identify the sources for reconstructing the ice sheet (ice stream) dynamics. For the deglaciation, we monitor the timing of break-up and retreat/re-advance. And for the Holocene, we reconstruct the ice floe drift pattern (from where the ice-rafted debris was originally deposited to the final depocenter, as exemplified by the present study). Once this pilot study on surface sediments is introduced, we will apply it to records with well-constrained age models from the western Svalbard margin and potentially the northern Barents Sea margin (Yermak Plateau) where changes in paleo-ice-stream dynamics can be reconstructed over time.

Interactive comment on Clim. Past Discuss., 9, 4145, 2013.

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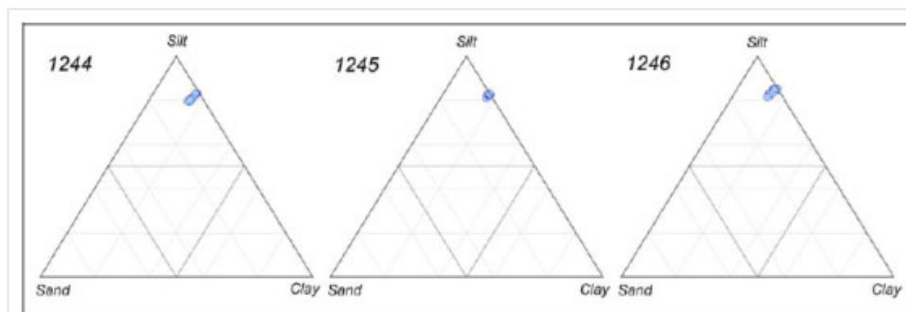


Fig. 1.

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