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Determination of sediment provenance by unmixing the mineralogy of source-area sediments: The "SedUnMix" program

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ABSTRACT

Along the margins of areas such as Greenland and Baffin Bay, sediment composition reflects a complex mixture of sources associated with the transport of sediment in sea ice, icebergs, melt-water and turbidite plumes. Similar situations arise in many contexts associated with sediment transport and with the mixing of sediments from different source areas. The question is: can contributions from discrete sediment (bedrock) sources be distinguished in a mixed sediment by using mineralogy, and, if so, how accurately? To solve this problem, four end-member source sediments were mixed in various proportions to form eleven artificial mixtures. Two of the end-member sediments are felsic, and the other two have more mafic compositions. End member and mixed sediment mineralogies were measured for the <2 mm sediment fractions by quantitative X-ray diffraction (qXRD). The proportions of source sediments in the mixtures then were calculated using an Excel macro program named SedUnMix, and the results were evaluated to determine the robustness of the algorithm. The program permits the unmixing of up to six end members, each of which can be represented by up to 5 alternative compositions, so as to better simulate variability within each source region. The results indicate that we can track the relative percentages of the four end members in the mixtures. We recommend, prior to applying the technique to down-core or to other provenance problems, that a suite of known, artificial mixtures of sediments from probable source areas be prepared, scanned, analyzed for quantitative mineralogy, and then analyzed by SedUnMix to check the sensitivity of the method for each specific unmixing problem.

1. Introduction

A common issue in many Quaternary studies is that of unraveling of sediment provenances along a depositional trajectory defined by transporting agents that could be rivers (Eberl, 2004), or icebergs and sea ice (Andrews et al., 2009). For example, changes in sediment provenance associated with transport away from glaciated margins has largely focused on sediments associated with North Atlantic Heinrich events and on sediment provenance during Marine Isotope Stages (MIS) 2 and 3 (Bond et al., 1992; Scourse et al., 2000; Grousset et al., 2001; Hemming et al., 2002; Farmer et al., 2003; Hemming, 2004; Peck et al., 2007; Darby and Zimmerman, 2008; Stein, 2008; Verplanck et al., 2009). Considerable emphasis has been placed on the application of radiogenic isotopic analysis to pinpoint the provenance of glacially derived (i.e. ice-rafted debris, IRD) sediments. However, such analyses are expensive, time consuming, and sometimes ambiguous (Grousset et al., 2000; Farmer et al., 2003). An alternative, cheaper approach, is to use quantitative X-ray diffraction (qXRD) of the non-clay and clay minerals in the sediment matrix (the <2 mm fraction, i.e. including sand, silt, and clay) (Vogt et al., 2001; Eberl, 2003; Moros et al., 2004; Andrews, 2008; Darby et al., 2011) (Fig. 1). The need to consider the <63 μm fraction, as well as the sand fraction in IRD studies, is essential as icebergs, and especially sea ice, make large contributions in the fine fraction (Andrews, 2000; Lisitzin, 2002; Stein, 2008; Dethleff and Kuhlmann, 2010).

The program SedUnMix, which is described more fully in Appendix A, calculates the contribution of each source area sediment to a mixed sediment using qXRD data. The first step is to measure accurately the quantitative mineralogy of each source and mixed sediment. We consider samples ($z_k = 1$ to p) to consist of minerals $i = 1$ to n and contributed from source regions x_j (maximum $j = 6$) with the same suite of minerals

$$\alpha_{j,k} * x_{i,j} \text{minimize} \longrightarrow \left(\text{abs.}|y_i - z_{i,k}|\right). \quad (1)$$

Weight% values are known for the source regions ($x_{i,j}$) and for the sample (z_i) (e.g. see Appendix A, Tables A–D) and SedUnMix seeks an iterative solution (Microsoft Excel Solver uses the Generalized Reduced Gradient algorithm) to optimize a nonlinear solution for the α_j coefficients (Eq. 1), which optimizes (i.e. reduces) the average absolute difference between the observed (z_i) and the calculated mineralogy (y_i). The sum of the absolute differences divided by 100 is called the degree

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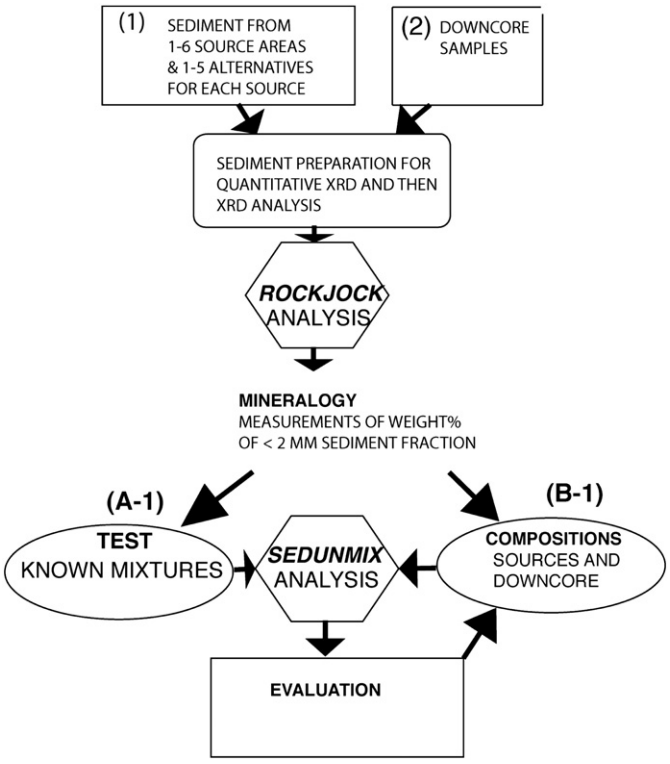

Fig. 1. Flow diagram showing the steps in the methodology from initial sample preparation, to quantitative X-ray diffraction analysis employing in this case RockJock (Eberl, 2003), to the sediment unmixing. This paper focuses on the experimental mixing as shown in A-1.

of fit (DOF) (Eberl, 2003) (Appendix A). The α_{φ} coefficients can vary between 0 and 1 and ideally sum to 1.0.

The question of how well this approach can discriminate between source regions is addressed in a series of experiments based on the mixing of four end member sediments, two of which are felsic, and two basaltic. In terms of the methods flow chart presented in Fig. 1, this paper focuses on the section labeled A-1 → SedUnMix → Evaluation.

2. Procedure

Samples that had been prepared and run for qXRD (Fig. 1) (see below, and Eberl, 2003), were selected from a series of grab samples on the shelf of east Baffin Island (cruise HU80028), from a piston core in Hamilton Inlet, Labrador (HU79018-109), a gravity core from above Denmark Strait (JM96-1216), and a box core from SW Iceland (MD99-2258) (Figs. 2 and 3) — hereafter the samples are referred to as: HU80, HU79, JM96, and MD99. The bulk sediment in the <2 mm sediments fraction from these largely glacial marine environments is dominated by non-clay minerals (Andrews et al., 2010a, 2010b; Andrews and Eberl, 2011) with only 10–30 wt.% being identified as clay minerals.

We note that any precise quantitative XRD method could provide the basis for the method we outline below (Ward et al., 1999; Vogt et al., 2001; McCarty, 2002; Moros et al., 2004), but here XRD scans are transformed into quantitative mineralogical data using the program RockJock, version 6 (Eberl, 2003). Using this program, carefully prepared mixtures of commercially purchased minerals could be resolved with a relative accuracy and precision of ±2% or better (J. Andrews, unpublished experiments). In addition, a comparison between qXRD estimates of total carbonate and coulometric measurements are virtually identical (Eberl, 2004). Sample preparation has been extensively modified in a later version of RockJock (v. 11), with the use of corundum rather than zincite as the calibration mineral, and with changes to the post-grinding sample treatment (see the latest RockMan manual at ftp://brrcrftp.cr.usgs.gov/pub/ddeberl/RockJock/). These subsequent changes in the RockJock program will improve the accuracy of mineral quantification over version 6 used here, and thereby likely improve the accuracy of SedUnMix calculations in future studies.

Five prepared samples from each of the four sources were combined, mixed, and run four times for qXRD determinations to ensure that adequate mixing had occurred. These are our "known end members." Thereafter, a series (n = 11) of known mixtures were prepared and run with qXRD (Table 1). All individual weight% values noted hereafter are in relation to the total species summing to 100%, and we are well aware of the complications associated with dealing with closed arrays (Chayes, 1971; Aitchison, 1986, 1992).

Conceptually, we consider our source areas to represent four glaciated regions that, through time, have delivered different proportions of sediment to an offshore site (Fig. 3). Since we know the proportions of the source sediments used to make the artificial mixtures (Table 1), the question is: can we determine their relative contributions by an analysis of sediment mineralogy? An additional caveat is needed: we expect that the sediment output from the source areas (Figs. 2 and 3) will have inherent variability (Fig. 4); hence, our efforts to unmix the samples and estimate errors must take this variability input into consideration.

2.1. Terminology

For clarity we define the two components of our investigation — mineralogy (Eq. 1, x_i) and sediment provenance (α_k). Mineralogy is used to designate the weight% (wt.%) of non-clay and clay mineral species in a sample, and is determined by qXRD using Rockjock v6 (Eberl, 2003). The observed or measured mineralogies are the results from a qXRD run, whereas the expected mineralogy is calculated (Table 2, Appendix Table C). Provenance defines the proportion of a various sediment sources (= end members) of sediment, and is calculated by SedUnMix (see below). The expected provenance is that defined by the known sediment mixtures (Table 1), whereas the observed composition is that calculated by SedUnMix. The approach embodied in SedUnMix carries with it the implicit assumption that there are no non-linear changes in mineralogy associated with transport distance.

3. Results

We first determine whether or not the mineralogies of the source areas are different, using Principal Component Analysis and Discriminant Function Analysis, and find that at least 3 of the 4 source sediments are statistically distinct in their mineralogy. Then we evaluate sample processing errors, and find, by repeated qXRD analysis, that such errors are minimal.

3.1. Evaluation of the end member data

An initial question is how different are the four areas in terms of their mineralogy? To answer this we performed a Principal Component Analysis (PCA) (Davis, 1986) on the log-ratio transformed data (Aitchison, 1986) (14 non-clay and 7 clay mineral species (Supplementary material)) to circumvent problems associated with a closed array (i.e. data sum to 100%). Calcite was excluded from the mineralogy because of its dual role in these areas—being detrital in some instances (Andrews and Tedesco, 1992), or a measure of in situ marine productivity in others (Andrews et al., 2001). The first two axes of the covariance PCA explained 45% of the variance with the 1st axis (27.2%), largely indicating a felsic to mafic gradient (Fig. 5A) with end points of quartz and pyroxene. The 2nd PC axis (17.5%) is strongly associated with negative loadings on Fe-chlorite and anorthoclase feldspar, and weaker positive