## Correspondence

Particle size and mineralogical composition of inorganic colloids in glacier-melting water and overlying ice in an Alpine glacier, Oberaargletscher, Switzerland

In many mountainous regions, glaciers are major erosional agents and therefore sources of suspended sediments in downstream rivers and lakes. As Hannah and co-workers recently pointed out in this journal (Hannah and others, 2003), numerous studies have been carried out into suspended sediments in proglacial streams, which have mainly focused upon characterizing weathering phenomena (Brown and others, 1994, 1996; Tranter and others, 2002) and estimating suspended-sediment loads (Collins, 1979; Warburton, 1990; Hodgkins, 1996; Willis and others, 1996; Richards and Moore, 2003). Research into the particle-size distribution and composition of suspended particles is very limited (Fenn and Gomez, 1989; Woodward and others, 2002). Colloids are particles that are several orders of magnitude smaller (1 nm-1 µm) than the more frequently studied 'suspended' particles (Filella, in press). However, in spite of their size, they are of major scientific interest because they have a high specific surface and thus carry substantial amounts of sorbed trace elements and organic micropollutants. Their behaviour and fate in water systems is clearly distinguishable from that of truly dissolved substances; most notably, their residence times are orders of magnitude larger than those of the 'suspended' fractions but, unlike truly dissolved metals, they can undergo relatively fast coagulation and sedimentation processes. Colloids are heterogeneous in size and composition, present in low concentrations (in mass units) and unstable. To our knowledge, no particle-size distribution or mineralogical composition data have been published for colloidal material released in meltwaters of Alpine glaciers. Similarly, although glacier ice is known to contain mineral particles (Benn and Evans, 1998), specific attention has not yet been paid to the characterization of the colloidal particles trapped in Alpine glacier ice. This may be explained, in part, by the difficulties involved in the quantitative assessment of the size and composition of colloidal materials.

As part of the study into the possible role of colloids in a lake ultra-oligrotrophy problem (Lake Brienz, Switzerland), ice and water samples were collected towards the cessation of the 2005 melt season from the Oberaargletscher termini (Berner Oberland, Switzerland; altitude 2305 m; 46°32′26″ N, 8°14′15″ E). The Oberaargletscher had a surface area of 5.82 km<sup>2</sup> and was 4.95 km long in 1973. Length variation measurements between 1858 and 2001 are available from http://glaciology.ethz.ch/swiss-glaciers/ glaciers/oberaar.html. The glacier lies on crystalline bedrock, mainly granite and common micaschist. An artificial lake (Oberaarsee, 1.46 km<sup>2</sup>, 0.06 km<sup>3</sup>) collects glacier meltwater. Glacier outlet stream and glacier surface meltwater samples were collected manually using thermostated bottles (2 L) at the portal of the glacier. Discharge and suspendedsediment concentrations on the sampling day represent endof-ablation-season values. The sampling day was very cloudy and slightly rainy. Samples were collected at midday. Two glacier ice samples (~2 kg each) were collected in polyethylene containers and placed in a thermostated box cooled with dry ice (-78.5°C) to be transported to the laboratory (taking about 6 hours). Ice was partially melted in an oven at  $60^{\circ}\text{C}$  just before analysis. Total suspended solids (TSS) were obtained by filtering a known volume of water through  $0.45\,\mu\text{m},\,50\,\text{mm}$  cellulose nitrate filters.

Particle-size distributions of colloidal particles in water and ice were measured with a single-particle counter (SPC) in the range 100–2000 nm on unfiltered samples. The instrument used (Particle Measuring Systems, Boulder, CO, USA) is composed of two single-particle counters: a high-sensitivity liquid in situ (HSLIS) monitor, M50, and a volumetric spectrometer, LiQuilaz-S02. Both measuring systems are based on the principle of light scattering by single particles. The technique and measuring procedure are described in detail in Rossé and Loizeau (2003). The main advantages of this measuring technique are the fact that it gives number-based particle-size distributions directly and it does not require any pre-treatment of the sample.

At the same time, the chemical composition and mineralogical composition of mineral colloids was assessed by transmission electron microscopy (TEM) coupled with energy-dispersive spectroscopy (EDS) and selected-area electron diffraction (SAED). Specimen grids were prepared using a non-perturbing procedure (Perret and others, 1991). A detailed description of the methodology used can be found in Chanudet and Filella (2006). One hundred particles were analysed for each sample. For this number of particles, statistical considerations indicate that results for particles present at less than 10% should only be considered as semi-quantitative.

Table 1 shows the results obtained for two different ice samples, glacier outlet stream water, glacier surface meltwater and a sample from the Oberaarsee. The different total solid concentrations in stream and lake waters reflect the rapid sedimentation of bigger particles in the lake. Interestingly, despite the significant difference in total particle concentration in these systems, they contained a similar number of colloidal particles. This implies that colloid concentration is related to particle origin (glacier abrasion of the bedrock) but is independent of the kinetic energy of the system (much higher in the stream than in the lake). Stream and lake colloid concentrations are much higher than those in ice and surface runoff samples. Even though the ice samples contained very different amounts of total suspended solids, there was little difference in colloid abundance and this does not reflect the level of variation in total solids. As observed in most natural waters (Filella, in press), the dependence of the measured number size distribution on particle diameter in all the samples studied could be expressed by a power-law dependence:

$$\frac{\mathrm{d}N}{\mathrm{d}d_{\mathrm{p}}} = Ad_{\mathrm{p}}^{-\beta},\tag{1}$$

where N is the particle number,  $d_p$  is the particle diameter, A is a coefficient related to the total number concentration of particles and  $\beta$  is the power-law slope. Irrespective of the total amount of solids present, the  $\beta$  values obtained for all water samples are quite similar. This implies both a common origin and the existence of similar colloid processes in waters of similar chemical composition. Slope values are much smaller for ice samples, which suggests that they contain more large colloids than water samples. This

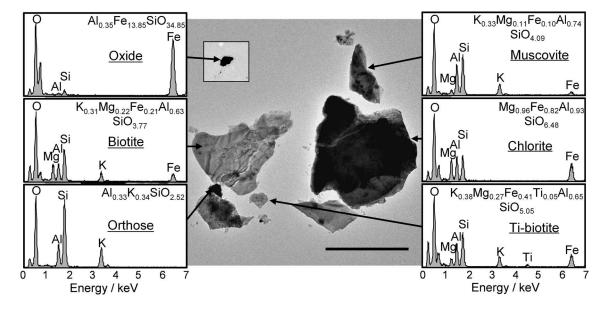
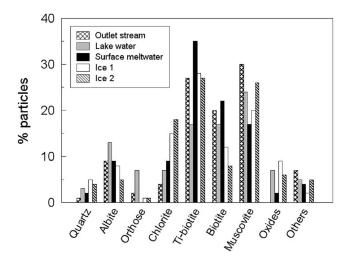


Fig. 1. TEM micrograph of some typical mineral colloids and their elemental composition determined by EDS. Scale bar: 2 µm.

difference can be attributed both to the existence of different particle-transport processes (i.e. very slow, if any, differential settling and sedimentation-like processes in ice) and to different colloid origins in ice and in water (i.e. aerial-mediated transport to the surface of the glacier and entrapment in newly formed ice in ice vs direct glacier abrasion in water).

Figure 1 shows a TEM micrograph of some typical mineral colloids found in the samples studied. The mineralogical composition of the main colloids present in the different samples is shown in Figure 2. Glacier-melting water was mostly composed of aluminosilicates, with a strong presence of Ti-rich biotite, biotite and muscovite, and smaller quantities of albite and chlorite. Some quartz and orthose particles were also present. This composition reflects the composition of the rocks underlying the glacier. Glacier surface meltwater has a similar composition, but with a slightly higher proportion of Ti-rich biotite and a lower proportion of muscovite. The trends identified in lake water are exactly the opposite, with significantly less Ti-rich biotite and more muscovite and albite. Globally, the composition of



**Fig. 2.** Mineralogical composition of inorganic colloids determined by combination of EDS and SAED.

these samples indicates that the origin of the colloids is mostly bedrock erosion.

The mineralogical composition of the colloids contained in the two samples of glacier ice can be said to be similar. These colloids are also composed mainly of aluminosilicates and are quite similar to the colloidal particles observed in water samples, although the proportions are different for some minerals: ice samples are very poor in orthose and significantly less rich in biotite but are comparatively rich in chlorite. Interestingly, ice samples contained oxide particles which were entirely absent from glacier-melting waters. They are low in number, and conclusions can only be drawn at a qualitative level. Both titanium and iron oxides were present. All iron-oxide particles contained significant amounts of K, Mg, Al and Si. Morphological considerations (non-globular shapes) seem to indicate that the iron-oxide particles consisted of aluminosilicate particles coated by iron oxyhydroxides. Some specimens of apatite, titanite, kaolinite, barite and calcite were also present.

We expect to extend the original, promising results presented here to the study of colloidal particle dynamics in bulk waters issued from glacier termini and in glacier ice over snowmelt- and ice-melt-related ablation periods and during precipitation events. We believe that adequately characterizing mineral colloids (size and chemical and mineralogical composition) will lead to a better understanding of particle source areas and supply regimes and to a better evaluation of the effect of glacier melting on downstream water systems.

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Table 1. Colloid size, number and mass characteristics

Sample	$oldsymbol{eta}^*$	Colloid number <sup>†</sup> mL <sup>-1</sup>	Colloid $mass^\ddagger$ $mgL^{-1}$	TSS <sup>§</sup> mg L <sup>-1</sup>
Glacier ice 1	$3.3 \pm 0.2$	$(4.08 \pm 0.10) \times 10^7$	$0.58 \pm 0.02$	$60.2 \pm 0.2$
Glacier ice 2	$3.0 \pm 0.2$	$(6.12 \pm 0.10) \times 10^7$	$1.31 \pm 0.04$	$105.0 \pm 0.3$
Glacier surface meltwater	$4.0 \pm 0.1$	$(9.93 \pm 0.03) \times 10^7$	$0.74 \pm 0.01$	$16.0 \pm 0.2$
Glacier outlet stream	$4.0 \pm 0.1$	$(1.01 \pm 0.01) \times 10^9$	$7.3 \pm 0.1$	$176.1 \pm 0.4$
Lake water	$4.2\pm0.1$	$(1.16 \pm 0.01) \times 10^9$	$8.4\pm0.1$	$59.5 \pm 0.5$

<sup>\*</sup>Slope of the power-law distribution (Equation (1)) and corresponding standard error obtained from linear regression analysis of the data.

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<sup>&</sup>lt;sup>†</sup>Measured in the range 100 nm–2  $\mu$ m. Given error = 1 SD.

 $<sup>^{\</sup>ddagger}$ Calculated in the range 100 nm-2  $\mu$ m, assuming a spherical shape and a density of 1.6 g cm<sup>-3</sup>. Given error = 1 SD.

<sup>§</sup>Total suspended solids.