Carbonate isotope preparation

Lake sediment samples are prepared for analysis of stable isotopes of carbon and oxygen in carbonate minerals by treatment with an oxidizer (typically bleach) to destroy organic matter that may interfere with the mass spectrometer. The bleach is rinsed out of the sample by repeated centrifuging and decanting until no further chlorine smell is detected. Before or after bleaching, samples may be sieved to remove larger particles, including sand, detrital carbonates, and ostracode shell fragments (the latter, microscopic crustaceans, usually inhabit a different isotopic environment in the lake than that in which authigenic carbonates are produced and thus should be separated and discarded). Typical lacustrine carbonate grains are <30μm, so 63μm steel sieves or various sizes (40 or 70μm) of Nitex screen fabric are appropriate to remove unwanted particles.

If splits of the samples are also to be analyzed for trace elements after bleaching, we advise using lab grade sodium hypochlorite (NaOCl) rather than commercial bleach. The latter is much cheaper (by a factor of ~100), but may contain any number of impurities and has been shown in Minnesota Isotope Lab/Core Lab tests to change the trace elemental composition (Mg, Sr, etc) of carbonates treated with it.

Procedure:

1. Put wet or dried sediment into 50mL centrifuge tubes. The mass spec takes very little carbonate to produce a number, so (depending on carbonate content) a 50-100 milligrams may be sufficient.
2. Fill to the 50mL mark with bleach/lab NaOCl solution. 50-50 bleach-water (~2.5% NaOCl) is the typical dilution.
3. Leave samples overnight (some researchers choose different times, from 1 hour to 24 hours; the emphasis should be on uniform treatment of all samples from a given core), shaking or vortexing once or twice during that time if possible.
4. Spin samples down in the centrifuge. 5 minutes at 3000 RPM should be sufficient, but settling should be gauged by eye: the supernatant (overlying liquid) should be clear, not cloudy. The supernatant may be colored (e.g., by the solution of organic compounds), but this is easy to distinguish from cloudiness caused by clay particles remaining in suspension. If the supernatant is cloudy, centrifuge longer. If it is clear, move on to the next step.
5. Decant either by pouring off the supernatant or "sipping" it using a vacuum-and-flask setup (see grain size SOP). In either case, be careful to stop pouring or sipping liquid before fine particles are swept up and lost.
6. Vortex before adding rinse water. The mixer works better when there is little overlying liquid. Occasionally it is necessary to break up the sediment pellet with a spatula; do this gently to avoid breaking sediment components.
7. Add deionized water to the 50mL mark. Some researchers use regular house DI water, but some prefer to use the high-purity Milli-Q DI.
8. Centrifuge again, decant, rinse. Repeat this sequence until you can no longer detect the smell of the bleach (chlorine, or swimming pool smell). Alternately, you can use pH

paper to determine when the solution has become neutralized, but the human nose is a more sensitive judge. Chloride can interfere with the mass spectrometer, so be sure it has all been rinsed out of the sample before stopping.

9. When samples are clean, screen if desired to remove large particles. Set sieves over 250mL beakers and rinse samples through. Return fine fraction (i.e., what has passed through the sieve) to centrifuge tubes and spin down again; discard coarse fraction or save for other analysis.
10. If not sieving, decant last rinse water but do not refill. Freeze and freeze-dry sediment. Tip sediment into a mortar and grind to homogenize. Enter sample list into project.xls (available from the Core Facility or the MN Isotope Lab) so that sample numbers can be generated by the database and samples can be submitted for analysis. Contact Stable Isotope Lab manager Maniko Solheid (maniko@umn.edu) for more information.

Materials:
50mL centrifuge tubes (multiples of 8)
Commercial bleach or lab grade sodium hypochlorite
250mL beakers
Sieves or screens
Stainless steel spatula

Equipment:
Brinkmann 3810 benchtop centrifuge (holds sixteen 50mL tubes)
Vortex Jr. mixer

Safety:
Lab coat
Goggles