Suitability of IAEA-603 as a replacement of NBS19 for small sample carbonate analysis

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The VPDB scale is anchored by NBS19 and LSVEC with absolute values for $\delta^{13}C$ [1]. For $\delta^{18}O$ values, the only carbonate material with an absolute value is NBS19 [2]. It is thus a critical reference material. NBS19-TS is now exhausted and IAEA is proposing IAEA-603 as a replacement, produced from Carrara marble. Most of the carbonate international reference materials are distributed with a grain size of about 200 to 500 µm to minimize water adsorption. Thus, the analysis of 100 µg of these international reference materials is often given by 1 grain resulting in less than desirable reproducibility. IAEA will not distribute smaller grain sizes due to possible isotopic exchange at a large surface area exposed to CO2 and moisture, and grinding by individual laboratories may result in heating and conversion of calcite to aragonite accompanied by a small but measurable fractionation. Here, we evaluate the suitability of IAEA-603 for calcium carbonate isotopic analysis at the 100 µg level. About 15 kg of ground and sieved material was uniformly divided into 31 bottles by IAEA. A subsample of each bottle was ground and sieved resulting in 4 differend fractions: i) the original material (200 to 500 µm), ii) a fraction <90 µm, iii) a fraction between 90 and 125 µm and iv) a fraction >125 µm. All 4 fractions were analyzed for $\delta^{13}C$ and $\delta^{18}O$ of all 31 subsamples on an Isoprime^{TM} triple collector IRMS in dual inlet mode coupled to a MultiCarb^{TM} system. Preliminary results show that average values vary little from one fraction to another (table 1). However, the largest standard deviations are obtained with the original material and the lowest one for the fraction of less than 90 µm. X-ray diffraction analysis of a subsample and all of its fractions shows that only calcite is present in all fractions. Following these preliminary results, IAEA has decided to wash the original material to remove the fine dust fraction, and subsamples of the washed material will be analyzed following the same protocol.

Table 1. Average $\delta^{13}C$ and $\delta^{18}O$ and standard deviations of all subsamples

	$\delta^{13}C$ ‰ vs VPDB	STDev (1σ)	$\delta^{18}O$ ‰ vs VPDB	STDev (1σ)
Grains	2,466	0,024	-2,437	0,038
<90	2,469	0,012	-2,405	0,027
90-125	2,461	0,016	-2,371	0,025
>125	2,455	0,021	-2,408	0,033
all	2,466	0,018	-2,406	0,038

[1] Coplen, T.B. & al. (2006) *Anal. Chem.* **78**, 2439-2441.
[2] Coplen, T.B. (1995) *Nature* **375#**, 285.

Mechanisms of chemical weathering: nanoscale-analytical measurements yield evidence for a weathering continuum

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Chemical weathering in the field occurs under complex conditions, characterized by variable degrees of aqueous chemical saturation and chemically complex fluids that may contain significant concentrations of ions, metals, ligand complexing agents, inorganic and/or organic acids or bases. In addition, weathering may also occur in very specific environments, such as in µm-sized pore spaces or in contact with mycorrhiza. Becasue of the complexity inherent to natural chemical weathering environments, it is not surprising that many types of alteration have been documented; two of the commonest reveal a) mineral-mineral replacement b) formation of amorphous, silica-rich surface layers. The question addressed in this talk is whether it is possible to define a unique nanoscale mechanism that controls chemical weathering.

Here we present recent measurements of the structure and chemical composition of mineral surface interfaces associated with the natural weathering of granite and serpentinite. The samples investigated were extracted from environments that are characterized by subaerial, shallow soil, and biological/abiological alteration. As detailed in a recent publication (Hellmann et al., 2012), one of the most promising techniques for studying chemical weathering at the nanoscale is based on sample preparation by focused ion beam (FIB), and measurements using high resolution transmission electron microscopy techniques, in particular HRTEM, STEM-HAADF, and EFTEM/EELS. The latter technique is particularly useful for providing nm-scale chemical maps of mineral surface interfaces.

The mineral surface interfaces that were investigated show evidence for spatially coincident and very abrupt structural and chemical changes (nm-scale sharp gradients) at the boundary between the unaltered parent mineral and the silica-rich amorphous surface layer. This type of chemical weathering was observed in all samples. The sharp structural and chemical boundaries that we measured are compatible with an interfacial dissolution-reprecipitation mechanism, and not solid-state volume interdiffusion associated with preferential cation loss and leached layer formation. Based on these results, as well as published studies on mineral-mineral replacement, we propose a chemical weathering continuum based on a dissolution-reprecipitation mechanism that unifies the different types of weathering observed in nature.

[1] Hellmann (2012) *Chemical Geology* **294-295**, 203-216.