Concentration and Behavior of CO_2 in MORB and OIB: a reevaluation

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Estimation of initial magmatic CO_2 contents in basalts is hindered by degassing and loss of CO_2 during magma ascent. The most widely accepted estimates of CO_2 flux are derived from ultra-depleted ([Nb]<1.5ppm) mid-ocean ridge basalts (MORB) and melt inclusions from Siqueiros region of the East Pacific Rise that did not exsolve CO_2 [1], and from highly vesicular Mid-Atlantic Ridge (MAR: 14°N) "popping rocks" that did not lose bubbles because they ascended quickly [2,3]. These data indicated that that CO_2/Nb was roughly constant at 239±46 for MORB and that CO_2 behaves incompatibly like Nb during melting and source enrichment [1]. A correct recalculation of the CO_2/Nb in popping rocks from 14°N, and new data from popping rocks at 34°N MAR, showed that their CO_2/Nb is much higher: closer to 576 [4]. These authors proposed that the low CO_2/Nb values for ultra-depleted MORB [1] are unrepresentative of the mantle. Their higher CO_2/Nb estimate [4] yields higher estimates of CO_2 flux from the mantle, in line with estimates from helium.

We have analyzed a larger set of ultra-depleted MORB glasses from the mid-ocean ridge system. Most erupted undersaturated in CO_2, have few or no vesicles, and yield extremely low CO_2 when crushed *in vacuo*. Their CO_2/Nb is 250±50, showing that this ratio [1] is widely applicable to ultra-depleted mantle. We also compiled published data for enriched submarine basalts including ridge popping rocks [4], and basalts from North Arch, Hawaii. The latter have up to 57% vesicles, suggesting two samples lost no bubbles [5]. Their CO_2/Nb is 1125 and 1216, similar to ratios for some popping rocks from 34°N. For the data set as a whole, CO_2/Nb is positively correlated with La/Sm. We propose that CO_2 is more incompatible than Nb, behaving geochemically more like Ba or Rb. CO_2/Ba is 114±43 for most ultra-depleted through highly enriched MORB. Rb and Ba should be better proxies for CO_2 because, unlike Nb, they are not retained in subduction zones during magma genesis. Thus, Rb and Ba more closely follow CO_2 during subduction and recycling into deep mantle. A Ba proxy for CO_2 suggests a MORB CO_2 flux that is ≈40% higher than [4] and ≈3x higher than [1].

[1] Saal et al. 2002 Nature 419. [2] Sarda & Graham 1990 EPSL 97. [3] Javoy & Pineau 1991 EPSL 107. [4] Cartigny et al. 2008 EPSL 265. [5] Dixon et al. 1997 J. Petrol. 38.

'Freiberg Strategy' for obtaining matrix-matched reference materials for resource-related microanalytical methods technology

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Quality assurance of natural raw materials (e.g. ores) requires thorough studies on concentration and spatial distribution patterns of technologically relevant trace elements within the mineral matrix at the microscale. Obtaining such a goal is yet only possible with the use of beam-based microanalytical methods and a proper set of homogeneous, matrix-matched reference materials (RMs) doped with trace elements relevant to resource technology.

Natural minerals usually exhibit chemical heterogeneity at μg/g sampling masses and are unsuitable as RMs for in-situ chemical microanalysis. On the other hand, available synthetic RMs (e.g. glasses, pressed pellets) fail to satisfy matrix-match criterion.

A collaboration involving several German scientific institutions centered around TU Bergakademie Freiberg proposed a novel strategy for obtaining such RMs through the synthesis of multi trace element doped mineral matrices subsequently tested for chemical and structural homogeneity with both microscopic and spectroscopic (RMs-dependent and absolute) microanalytical methods.

Three mineral matrices vital to resource technology applications – pyrite, tantalite and feldspar – have been synthesized using flux method, Czochralski method and alkoxide-based sol-gel synthesis, respectively and doped with various sets of technologically important trace elements at the concentration range found in corresponding natural minerals. Their spatial chemical micro-homogeneity has been investigated using light and electron microscopy as well as RMs–dependent (EPMA, LA-ICP-MS) and absolute (PIXE, PIGE) analytical methods.

Quantitative and qualitative elemental spatial distribution maps have been obtained for major and trace elements for each matrix. Homogeneity of the matrices was evaluated using petrologically sensitive statistical analysis.

Established homogeneity testing protocol will be employed in the next stages of the project.