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**TITLE:** Fluorine in the Mantle: the Role of Nominally Anhydrous Minerals

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**ABSTRACT BODY:** Analyses of fluorine in hydrous minerals such as amphiboles, micas, and clinohumite, as well as apatite, form the basis for classic studies of F distribution within the mantle [1]. An explicit assumption of this work is that the common nominally anhydrous minerals (NAMs) in the mantle – olivine (ol), garnet (gt), ortho- and clinopyroxene (opx and cpx) – do not contribute significantly to its bulk F content. New studies [2,3,4] using secondary ion mass spectrometry (SIMS) are beginning to challenge this assumption in the same way that, about two decades ago, infrared studies of NAMs [5] changed perceptions about the distribution of hydrogen in the mantle and paved the way for increased understanding of the critical role of trace amounts of volatiles on geophysical processes within the deep Earth as well as other planets.

In this work, we used SIMS to measure H and F in NAMs derived from three different mantle regions (the Colorado Plateau, the Rio Grande Rift (Kilbourne Hole), and the South African cratonic mantle), as well as in samples of crustal origin. Highly precise measurements of F with very low detection limit (0.1 ppm) are easily achieved using SIMS, although accurate quantification suffers from uncertainties that we will discuss in detail (e.g., heterogeneity in glass standards, matrix effects). We have also taken precautions to screen out contributions to analyses from F-bearing, nanometer-scale phases such as amphibole lamellae or fluid inclusions [6]. Regardless of these analytical issues, we find the following:

1) F concentrations are distinctly lower in xenocrysts from the Colorado Plateau (ol and opx <1 ppm, gt 0.2-3 ppm, cpx 8 ppm) compared to samples from Kilbourne Hole (opx 7 ppm, cpx 46 ppm) and from South African kimberlites (ol 6-47 ppm, gt 3-10 ppm, opx 12-17 ppm, cpx 9-36 ppm). This suggests that mantle F reservoirs vary and are not necessarily coupled to H.

2) Measured concentrations suggest that F is more compatible in olivine than indicated by experimental studies [3,4,7], which consistently find mineral-melt partition coefficients following the order  $cpx > opx > ol$ .

3) Contrary to the study of Beyer et al. [3] but in accord with the results of Dalou et al. [4], we find no overall correlation between Al and F in pyroxenes.

4) Results so far suggest that H and F co-substitute in garnets, but are decoupled in other NAMs.

Beyer et al. [3] have suggested that the F budget of the mantle can be entirely accommodated by F incorporation in NAMs, and our results are in accord with their calculations. We speculate that F within mantle NAMs may exert an important influence on melting, but probably has much less of an effect compared to hydrogen – or even no effect at all – on other processes or properties such as deformation, chemical diffusion, viscosity, and electrical conductivity.

[1] Smith et al. (1981), *Lithos*, 14, 133-147. [2] Hervig and Bell (2005), Fall AGU 2005 abstract [3] Beyer et al. (2012), *EPSL*, 337-338, 1-9 [4] Dalou et al. (2012), *CMP* [5] Bell and Rossman, 1992, *Science*, 255, 1391-1397 [6] Mosenfelder et al. (2011), 96, 1725-1741. [7] Hauri et al. (2006), *EPSL*, 248, 715-734.

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