

Problematic features with Ko et al. (2022, Nature, Nov. 3): Ca-dissolution in bridgmanite

Mineral abbreviations. **bm**, bridgmanite; **pbm**, post-bm; **dm**, davemaioite (previously: perovskite-structured CaSiO₃), **fp**: ferropericlasite

The experimental results of Ko et al. (2022) contradict all previous experimental phase relation results, from both subsolidus and melting studies. Although I cannot find any specific problems with the experiments performed by Ko et al., the results should be verified by further independent studies.

In their Extended Data Fig. 1 (ED Fig. 1), they partly misrepresent and partly omit previous experimental results. An example of this may be the four experiments reported in Table 1 of Sinmyo & Hirose (2013, PCM) at pressures of 28, 82, 109 and 114 GPa. Whereas bm- and fp-compositions are reported for all four experiments, dm-compositions are reported only for those at 28 and 82 GPa. The table does *not explicitly imply* that dm was absent in the two highest pressure experiments. The bm in all of the four experiments have low CaO-contents of 1.0, 2.7, 2.8 and 1.1 wt%, respectively, indicating that dm was in fact present in all of them. In contrast, the Ko et al. (2022) ED Fig. 1 shows the two highest pressure results as dm-free assemblages. The reason that dm was not reported from the highest pressure products from the smallest culet and sample chamber type of Sinmyo & Hirose (2013), might be that these are very fine-grained products. The observation and microanalysis of dm in fertile (pyrolytic) and depleted peridotites are challenging (especially in the highest pressure and most fine-grained materials), because the dm-proportions are only about 5.6 and 1.7 %, respectively, in such lithologies.

Here I summarise several irregularities and apparent mistakes in ED Fig. 1:

1. ED Fig. 1 misrepresents at least three of the four studies that Ko et al. label as dm-free run products. Ono et al. (2005, JGR), Ono & Oganov (2005, EPSL), Sinmyo et al. (2013, PCM) and Lobanov et al. (2020, EPSL) *do report* the presence of dm, whereas Lee et al. (2004) state that “Due to the consequently weak diffraction peaks of calcium perovskite, and overlap of diffraction peaks with those of the more abundant phases, cpv was not detected above ~70 GPa even though its stability has been documented to much higher pressures.” The reported bm-compositions of Lobanov et al., formed at 56 GPa and up to 2800 K, have low CaO contents of 2.38 cation% (average of 16 analyses). The Sinmyo et al. (2013) analyses are mentioned above. [In the ED Fig. 1 legend, it is unclear which references “Ono2005a” and “Ono2005b” refer to.]
2. ED Fig. 1 omits several important experimental studies, including the melting experiments on basaltic compositions by Pradhan et al. (2015, EPSL) and Tateno et al. (2018, JGR), which resulted in well-crystallised semi-concentric zones around the central ellipsoids of quenched melt, involving dm (primary liquidus phase), followed by silica and an outermost zone of bm, in contact with the recrystallized surrounding bulk basaltic lithology. The well-crystallised semi-concentric and monomineralic zones appear to have grain sizes exceeding 300-500 nm, well suited for clean chemical analyses by FE-EMPA or ATEM. Despite its spatial contact with the subsolidus bulk basaltic lithology, which has higher Ca-content than the quenched melt, the bm has Ca-content below 1-4 cation% (Pradhan et al: <1%, Tateno et al: <4%), in contrast to 8-10 cation% in the Ca-rich bm of Ko et al. In terms of peridotite melting experiments where bm is the first liquidus phase (e.g. Tateno et al. 2014, JGR; Nomura et al. 2014, Sci.; Caracas et al. 2018, EPSL – not in ED Fig. 1, either), the low Ca-content of the bm could possibly be ascribed to bm-melt partitioning. Pbm has generally even lower Ca-content than bm.
3. The illustrative and comparative melting experiments by Kuwahara et al (2018, PEPI) on peridotitic and basaltic compositions at 25 and 27 GPa in the 2398-2673 K range, as well as the experiments on basaltic bulk compositions of Hirose et al. (1999, Nat), Ono et al. (2001, EPSL), Hirose & Fei, (2002, GCA), Hirose et al. (2005, EPSL), Litasov et al. (2005, PEPI) and Ishii et al. (2022, EPSL), are also omitted from ED Fig.1. Most of the experiments in Kuwahara et al. (2018), Hirose et al. (1999) and Hirose & Fei (2002) are high-T and/or partial melting experiments, where near-solidus bm coexists with dm, which is mostly located in contact with the quenched melt. In spite of this, all of the bm-analyses in all of the seven experimental studies have low CaO-contents of 0.3-1.9 wt% (except one of the Ishii et al. (2022) bm-analyses with 3.11 wt% CaO).
4. ED Fig. 1 also omits Kesson et al. (1998, Nat), reporting low-Ca bm coexisting with dm in peridotite up to 100 GPa at near-solidus conditions, as well as Kesson et al. (1994, Nat), reporting low-Ca bm and low-Ca pbm with abundant dm in a basaltic composition at 75-135 GPa. Temperatures were not determined instrumentally in the two Kesson et al. articles, but Fig. 1 in Kesson et al. (1998) demonstrates that the analysed peridotite minerals formed at 70 GPa represent a near-solidus assemblage.
5. In addition to the omitted experimental studies, ED Fig. 1 misrepresents the temperature conditions of the seven Ricolleau et al. (2010, JGR) experiments on a basaltic composition, which were heated stepwise, with XRD-recording at each step, to within the 2398-2693 K range, before quenching to room T (Table 2). In spite of these high temperatures, which are marked at erroneously low values in ED Fig. 1, the reported bm-analyses (from run products quenched from the final high-T conditions) have low CaO-contents of 2.7-3.3 wt%, corresponding to 2.6-3.4 cation% Ca.