

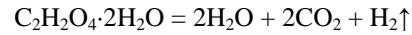
WATER-UNDERSATURATED NEAR-LIQUIDUS PHASE RELATIONS OF YAMATO 980459: PRELIMINARY RESULTS. D. S. Draper, Astromaterials Institute, University of New Mexico, Albuquerque NM 87131. david@draper.name

Summary: The liquidus of the Yamato 980459 (Y98 hereafter) bulk composition determined under water-undersaturated conditions with a mixed H₂O-CO₂ fluid (50%-50% molar, 29%-71% weight) is lowered by at least 200°C at 0.8 to 1.5 GPa compared to previously-determined anhydrous relationships, and the multiple-saturation point (MSP) between liquid and olivine + pyroxene may be constrained to move to higher pressure. If the MSP pressure represents the depth of origin for Y98, and that depth corresponds to the interface between the lower martian crust and upper martian mantle, then the presence of several percent water in the Y98 upper-mantle source could allow the martian crust to be somewhat thicker, and the temperature of melt generation substantially cooler, than if that source were anhydrous.

Introduction: Y98 is the most magnesian martian basalt thus far described. It has a severely depleted light rare earth element pattern [1] and has been shown experimentally to represent a liquid composition [2]. It may also reflect reduced conditions in its source [3]. It is thus of great interest in constraining the nature of the martian mantle. Dalton et al. [4] reported multiple saturation between Y98 melt, olivine, and low-Ca pyroxene under nominally anhydrous conditions at ~1.2 GPa and 1560°C, although similar experiments by Norris and Herd [5] showed a liquidus ~100-150°C cooler with the MSP possibly at ~1.5 GPa.

Given the strong interest in the role of water on Mars, and recent suggestions of up to several percent water in sources for some martian basalts [6], this study is designed to investigate the effect of small water contents on the phase relations of Y98 at elevated pressures. This abstract reports preliminary results from this volatile-bearing experimental study.

Experimental approach: The inverse experimental approach was employed, in similar fashion to the anhydrous work cited above, in which near-liquidus mineralogy of Y98 was determined at 0.8 to 1.5 GPa. In these runs, 25 to 30 mg of the same Y98 glass powder used in the studies of [2] and [3] (generously shared by G. McKay) was sealed into Au₇₅Pd₂₅ capsules (to minimize Fe loss) along with approximately 7 wt. % oxalic acid dihydrate powder, C₂H₂O₄·2H₂O. This material was chosen because it is much easier to weigh precise quantities to achieve desired water contents than is the case when using a microsyringe. Oxalic acid dihydrate decomposes to water and carbon dioxide at run conditions by the reaction



Assuming the H₂ produced diffuses out of the capsule (AuPd should be nearly transparent to hydrogen), this reaction produces a fluid composed of 50 mol% H₂O and 50 mol% CO₂, or 29 and 71 wt%, respectively. Thus adding 7 wt% oxalic acid dihydrate adds 2.03 wt% H₂O and 4.97 wt% CO₂ to the charge. At the pressures of these experiments, CO₂ solubility is <1 wt% [7], so these runs are undersaturated with respect to water but oversaturated with respect to CO₂. This low solubility suggests that the presence of excess CO₂ will have little effect on phase relations; but because Mars is also a CO₂-rich planet, its presence may in fact enhance the relevance of these results. In any case, at this juncture no direct effects of CO₂ have yet been determined, as outlined below.

Welded capsules were surrounded with 10-15 mg of powdered pyrophyllite, which has been shown to virtually eliminate water loss at these concentrations when using AuPd capsules [8]. Water loss was also minimized by using a comparatively oxidized starting material (the glass was synthesized at 1500°C in air for 24 hr, L. Le, pers. comm.), as determined by Hall et al. [9]. Oxygen fugacity (*f*O₂) at run conditions thus can only be estimated at this point, but by analogy with other hydrous work [10] is probably near FMQ. This is admittedly more oxidized than the IW+1 or so thought to typify the Y98 source [3], but buffering *f*O₂ under water-undersaturated conditions is very challenging, so this simpler approach was taken at the outset.

Capsules were run in UNM's High Pressure Laboratory QuickPress piston-cylinder device (manufactured by Depths of the Earth Co.) in salt-pyrex cells with crushable MgO inner parts. Temperatures were measured by type C W-Re thermocouples and controlled with a Love automated controller. Successful run products were mounted in epoxy, ground, and polished for electron microprobe analysis.

Results: This preliminary report describes nine successful experiments at ~2 wt% H₂O and ~5 wt% CO₂. Five of these produced quenched melt only, and the other four produced near-liquidus olivine (Fo₇₉₋₈₄) with Mg-chromite inclusions. Quenching Y98 from high pressure in the presence of volatiles does not produce glass despite quench rates of 200-300°/sec; this difficulty is similar to that reported for this starting material by McKay et al. [3]. Instead, liquids quench to very fine-grained mats of olivine, strongly zoned

low-Ca pyroxene, and Mg-chromite surrounded by small (10-15 μm) patches of evolved glass. Olivine phenocrysts are easily distinguished from quenched melt by their much larger sizes, and are quite homogeneous except for thin rims formed on quench, which show up bright in backscattered electrons (Fig. 1). The presence of fluid is confirmed both by the much lower temperature for olivine stability compared to anhydrous experiments and by the presence of vesicles formed by CO_2 vapor at run conditions. It is also indicated by the compositions of the small glass patches, which have much higher contents of SiO_2 , Al_2O_3 , and CaO , and much smaller contents of FeO and MgO , than does the starting material; these glass patches yield microprobe totals of only ~ 90 wt%, suggesting the original ~ 2 wt% H_2O was concentrated in these patches. Broad-beam analyses of the quench mats give totals of 95-98%.

Pressure-temperature conditions and phase relations for are shown in Fig. 2, where they are compared with anhydrous results [4, 5]. Subliquidus runs (e.g. Fig. 1) consist of 90-95 wt% quenched melt. Note that the liquidus at 0.8 to 1.5 GPa is $\sim 250^\circ\text{C}$ cooler than that reported by [4] and $\sim 150^\circ\text{C}$ cooler than that of [5]. Additional experiments are required to constrain whether the MSP reported by [4] persists, and the extent to which the olivine phase volume is expanded by the addition of water. These should be completed between abstract submission and the time of the meeting.

The most magnesian olivine grown in these water-bearing runs is Fo_{84} , very close to that in the natural meteorite. As in these experiments, inclusions of chromite in olivine are also common in the meteorite [11], suggesting it co-crystallized with olivine or even preceded it [12]. However, Mg-chromite in these runs is much richer in FeO (40-50 wt% vs. ~ 17 wt%) and poorer in Cr_2O_3 (28-32 wt% vs. ~ 57 wt%) than is chromite in the natural sample. This mismatch may be a consequence of the comparatively high $f\text{O}_2$ in these runs. Finally, the preponderance of low-Ca pyroxene in the quench mats in these charges suggests that this phase will be the next to crystallize at lower temperatures, as in the anhydrous case. No hydrous mineral phases have been detected thus far, either as phenocrysts or in the groundmass.

Discussion and next steps: The expected expansion of olivine's primary phase volume by the addition of water should push the MSP to higher pressure than was found dry; certainly the water-undersaturated results thus far preclude its shifting to lower pressures. If the MSP corresponds to the martian crust-mantle boundary region, then a deeper MSP suggests thicker martian crust. The presence of water in the source would permit Y98 melt to be generated at hundreds of

degrees cooler temperatures. This difference should have significant effects on thermal structure models of the martian mantle such as those of Kiefer [13].

Additional work in this study will include extension of coverage to ~ 2.0 GPa at this water content, increasing to larger water contents, and a better treatment of $f\text{O}_2$ in the experiments. One goal is to determine whether a near-liquidus phase can be stabilized under volatile-bearing conditions that could partition trace elements in such a way as to explain the severe depletions in Y98 and other shergottites such as QUE94201.

References: [1] Shirai, N. and Ebihara, M. (2004) *Ant Met Res*, 17, 55 [2] Koizumi, E., et al. (2004) *LPS*, XXXV, 1494 [3] McKay, G., et al. (2004) *LPS*, XXXV, 2154 [4] Dalton, H. A., et al. (2005) *LPS*, XXXVI, 2142 [5] Norris, J. R. and Herd, C. D. K. (2006) *LPS*, XXXVII, 1787 [6] McSween, H. Y., Jr., et al. (2001) *Nature*, 409, 487 [7] Pan, V., et al. (1991) *GCA*, 55, 1587 [8] Freda, C., et al. (2001) *Am Min*, 86, 234 [9] Hall, L. J., et al. (2004) *Min Mag*, 68, 75 [10] Draper, D. S. and Green, T. H. (1997) *J Pet*, 38, 1187 [11] Ikeda, Y. (2004) *Ant Met Res*, 17, 35 [12] Mikouchi, T., et al. (2004) *Ant Met Res*, 17, 13 [13] Kiefer, W. S. (2003) *MAPS*, 39, 1815

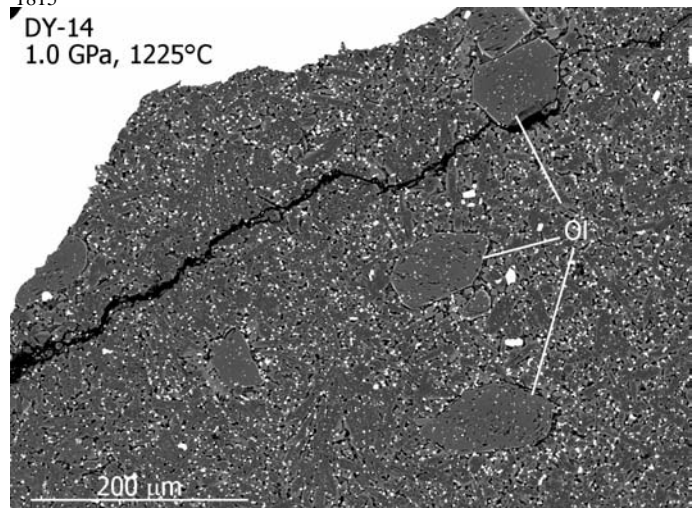


Figure 1. Backscattered electron image showing olivine (bright spots are Mg-chromite inclusions) in fine-grained quenched melt

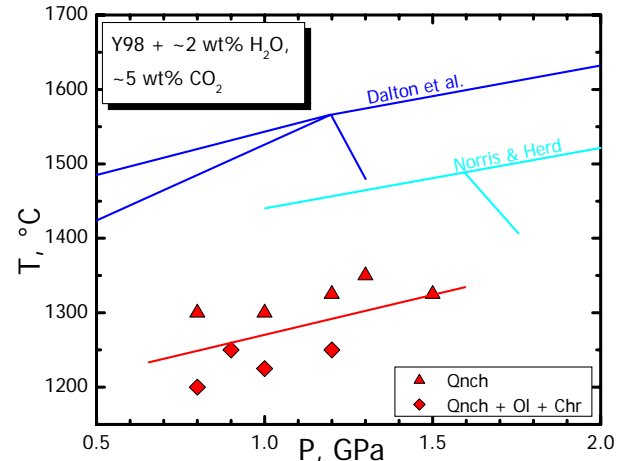


Figure 2. P-T summary diagram comparing water-undersaturated phase relations with anhydrous results of Dalton et al. [4] and Norris and Herd [5]. Qnch, quenched melt; Ol, olivine; Chr, Mg-chromite.