## The effect of post-entrapment crystallization on the $H_2O$ and $CO_2$ concentrations of rhyolitic (silica-rich) melt inclusions, and implications for magma degassing paths

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Concentrations of H<sub>2</sub>O and CO<sub>2</sub> in silicate melt inclusions (MI) are often interpreted to represent magmatic "degassing paths," in which depressurization of the magma during ascent leads to vapour saturation and release of CO<sub>2</sub> and H<sub>2</sub>O from the melt (e.g., Lowenstern, 1994). This interpretation requires that melt inclusions are trapped under conditions of vapour saturation at various locations (depths) along the ascent path. If the trapped melt is saturated in volatiles, then the melt must exsolve a volatile phase if any postentrapment crystallization occurs. As a result, the pressure inside the MI may differ from the confining pressure during post-entrapment cooling, and the PT path of the MI may be calculated knowing the solubility of H<sub>2</sub>O and CO<sub>2</sub> in the melt as a function of T and P, as well as the PVT properties of the H<sub>2</sub>O-CO<sub>2</sub> volatile phase, the partial molar volumes of H<sub>2</sub>O and CO<sub>2</sub> in the melt, and the molar volumes of the melt phase and the crystallizing solid phase. Using PVTX data for the systems NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O (Burnham and Davis, 1974) and NaAlSi $_{3}O_{8}$ -H $_{2}O$ -CO $_{2}$  (Holloway and Blank, 1994), we investigate the effect of small fractions of post-entrapment crystallization on the dissolved volatile content in an albitic melt inclusion entrapped under conditions of volatile saturation. The model is constrained to be a closed, isochoric system. As small amounts of albite crystallize on the inclusion walls, the melt becomes supersaturated in volatiles, and so nucleation and growth of an H<sub>2</sub>O, CO<sub>2</sub> or H<sub>2</sub>O-CO<sub>2</sub> vapour bubble occur and the pressure inside the MI is estimated from the difference between the molar volume of the volatile phase and the partial molar volume of the volatile in the melt using the EOS for H<sub>2</sub>O-CO<sub>2</sub> (Holloway, 1977; Flowers, 1979).

Significantly different styles of PT and volatile evolution occur in MI that are saturated



Fig. 1. Schematic PT trajectories followed by vapour-saturated MI during post-entrapment crystallization. Melt-volatile phase relations are shown by the  $H_2O$ - and  $CO_2$ -saturated solidus curves. The solid circle shows the PT point of entrapment of an  $H_2O$ -saturated melt inclusion at the same pressure (dashed line) as a  $CO_2$ -saturated melt inclusion shown by the solid square. Thick curves with arrows show the PT paths followed by both MI during PEC. The inset shows the PT path of a mixed  $H_2O$ -CO<sub>2</sub> saturated MI trapped at the PT point shown by the star, with isopleths of  $H_2O$  in the vapour phase shown as dashed lines).

with an H<sub>2</sub>O-rich fluid versus a CO<sub>2</sub>-rich fluid at the time of entrapment (Fig. 1). The differences are due to 1) the higher density of free CO<sub>2</sub> compared to H<sub>2</sub>O at magmatic PT conditions, and the larger partial molar volume of CO<sub>2</sub> compared to H<sub>2</sub>O in the melt phase; 2) the lower solubility of CO<sub>2</sub> compared to H<sub>2</sub>O in the melt phase; and 3) the negative dP/dT slope of the H<sub>2</sub>O-saturated solidus compared to the positive dP/dT slope of the CO<sub>2</sub>-saturated solidus (Fig. 1). As a result, for CO<sub>2</sub>-rich compositions the pressure in the MI and the dissolved CO<sub>2</sub> content of the melt phase both

decrease during post-entrapment crystallization. For  $H_2O$ -rich melts, the pressure and the dissolved  $H_2O$  concentration in the melt phase both increase during post-entrapment crystallization. Because the solubility of  $CO_2$  in the melt is much lower than that of  $H_2O$ , MI with mixed  $H_2O$ - $CO_2$  initial volatile compositions undergo a transition from pressure decrease to pressure increase during post-entrapment crystallization, and the  $H_2O$  concentration in the exsolved volatile phase increases as crystallization proceeds (Fig. 1).

The evolution of  $H_2O$  and  $CO_2$  contents in the melt (glass) phase during post-entrapment crystallization of volatile saturated MI in some cases reasonably reproduces the observed distribution of  $H_2O$ - $CO_2$  contents of natural MI (e.g., Fig 2). In particular, the dissolved  $CO_2$ content in MI is highly sensitive to small fractions of post-entrapment crystallization, such that nearly all the dissolved  $CO_2$  in the melt phase can be lost during crystallization of a few percent of the melt.

Model results show that dissolved volatile contents in the melt vary in a systematic manner during low degrees of post-entrapment crystallization. More importantly, the H<sub>2</sub>O and CO<sub>2</sub> contents of the melt (glass) in the inclusion define trends similar to those produced during opensystem degassing. Furthermore, the model predicts that the dissolved CO<sub>2</sub> in the melt phase may be almost completely lost to the vapour phase post-entrapment crystallization, durina even though the vapour bubble occupies less than one volume percent of the melt inclusion (Fig. 2). Thus, melt inclusions that all trap a vapour-saturated melt with the same volatile concentrations, but experience varying degrees of post-entrapment crystallization on the walls, will define an H<sub>2</sub>O-CO<sub>2</sub> concentration trend resembling an open-system degassing path.



Fig. 2. H<sub>2</sub>O-CO<sub>2</sub> contents of MI from Pine Grove, southwest Utah (solid circles, L'94 = Lowenstern, 1994; dashed curve, O-S degas. = open-system degassing; PEC = post-entrapment crystallization). Dashed curve represents open system degassing of a rhyolitic magma at 675 °C from Lowenstern (1994), and solid curve represents postentrapment crystallization of a rhyolitic ΜI entrapped at 877 °C, calculated in the present study. Both trends start at 4 kbars. For postentrapment crystallization, open circles show where the vapour bubble occupies 0.5 and 1 percent of the MI volume. Tic marks and numbers (5, 10, 15, 20%) on the PEC path show the proportion of the melt that has crystallized during PEC.

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