OXYGEN FUGACITIES IN THE SOLAR NEBULA DURING CRYSTALLIZATION OF FASSAITE IN ALLENDE INCLUSIONS:

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The oxygen fugacity under which primary phases in Ca-, Al-rich inclusions (CAI) equilibrated places an important constraint on their origin, as f_{O_2} is a direct measure of the composition of the gas phase with which CAI coexisted. Previous attempts to estimate f_{O_2}'s for CAI (1-4) were either indirect or yielded crude upper bounds. Moreover, they resulted in a tremendous range of over ten orders of magnitude in estimated f_{O_2}'s, from those more reducing than a gas of solar composition (1) to those more oxidizing than the QFM buffer curve (2). We present results of equilibration experiments under extremely reducing conditions on bulk compositions relevant to Type B inclusions. These are used to determine the f_{O_2} dependence of two oxygen buffer reactions involving the assemblage fassaite(Fass) - melilite(Mel) - spinel(Sp). Since this assemblage is common in Type A (5) and B (6) inclusions these results are used to determine the f_{O_2}'s under which the major phases in CAI equilibrated.

Three starting compositions were used: B1-1, B2-1 (7) and ETEG (CaO, MgO, Al_2O_3, SiO_2, TiO_2 = 32.3,6.7,18.4,36.3,6.4 wt%). The first two are synthetic analogs of a natural Type B1 and B2 inclusion, resp. The third was chosen to have a large amount of modal Fass. Chips of glass or glass + Sp were placed in Ir-wire cages and suspended in a furnace under a flowing gas for 1/3 - 63 hrs. Oxygen fugacity was controlled by bubbling an 85 vol% N_2 - 15% H_2 gas through an H_2SO_4-H_2O solution. This fixed $P(H_2)/P(H_2O)$ at 9600±2500, corresponding to a log f_{O_2} of -19.4±.3 at 1223°C. The H_2/H_2O ratio was checked for the Cr-Cr_2O_3 buffer using an intrinsic cell and reversing the equilibrium phase assemblage.

The crystallization sequence for B2-1 at low f_{O_2} is Sp+anorthite(An)>(1262°C), Fass+Mel(1244-62), while that for ETEG is Fass (1234-42), Mel+An+perovskite(Pv)(1229-1234), wollastonite(Wo)(1193-1209). Only one experiment was run on B1-1, so the equilibrium crystallization sequence could not be obtained for that composition. Crystallization temperatures in low f_{O_2} experiments are within 15 degrees of those for experiments conducted in air, suggesting that f_{O_2} does not have a major effect on crystallization sequence in Type B inclusions, as concluded in (4) from experiments at higher f_{O_2}. Both synthetic and natural Fass are solid solutions of Di($CaMgSi_2O_6$), CaTs($CaAl_2SiO_6$), T_3P($CaTi^{3+}AlSiO_6$) and T_4P($CaTi^{4+}Al_2O_6$). Ti^{3+}/Ti^{4+} in Fass was calculated from EPMA on the basis of one Ca cation and 6 oxygen anions per formula unit. Ti^{3+}/Ti^{4+} in synthetic Fass ranges from 0.5 to 3.1, with X_{Di}=0.4-0.7 and X_{CaTs}=0.16-0.25. Synthetic Fass compositions are within the range of those in Type B inclusions. Synthetic Mel is on the Gehlenite(Ge)-Akermanite(Ak) binary in the range Ak36-73, with Ak generally increasing with decreasing T for a given composition. Synthetic Sp is pure $MgAl_2O_4$.

Two O_2-producing reactions can be written for coexisting Fass+Mel+Sp in CAI. These are (A) $4T_4P+4Di = 4T_3P+2Ak+2Sp+O_2$ and (B) $4T_4P+2CaTs+2Di = 4T_3P+2Ge+2Sp+O_2$. The equilibrium oxygen fugacity for A can be determined from the free energy of reaction by

$$\log f_{O_2}\ (A) = \frac{-G_A^{o}}{2.303RT} - \log \frac{(a_{T_3P}^{Fass})^4 (a_{Ak}^{Mel})^2 (a_{Sp}^{Sp})^2}{(a_{T_4P}^{Fass})^4 (a_{Di}^{Fass})^4}$$

where G_A° is the free energy of reaction A for pure end-member phases and a_i^J is the activity of component i in phase j. An analogous expression can be written for reaction B. G_A° and G_B° were calculated from the known oxygen fugacity and phase compositions for one run on the B1-1 bulk composition, four on B2-1 and four on ETEG. Values of a_{Di}^{Fass} and a_{CaTs}^{Fass} were obtained using Margules parameters for the Di-CaTs join from (8). The activity ratio for T_3P/T_4P was calculated using a symmetric Margules parameter of 25±5 kcal/mole, estimated from our data on Fass-melt equilibria.

1986LPI....17...36B

It was assumed that $a_{Sp}^{Sp}=1$ and $a_{l}^{Mel}=X_{l}^{Mel}$. This leads to $G_A^\circ=128.8\pm2.0$ and $G_B^\circ=122.1\pm2.1$ kcal/mole at 1500K. The difference in free energy of formation $G^\circ(T_4P)-G^\circ(T_3P)$ is 17±2 kcal/mole at 1500K. An estimate of $G^\circ(T_4P)=-591\pm1$ kcal/mole was obtained from one experiment with the assemblage Wo+Pv+Fass at 1460K, so that $G^\circ(T_3P)=-608\pm2$ kcal/mole at 1500K.

Using our experimental determinations of G_A° and G_B°, f_{O_2} can be calculated from compositions of coexisting phases in natural inclusions. Such f_{O_2} values are strongly dependent on Fass composition but only weakly dependent on X_{Ak}. The difference in calculated log f_{O_2} between Fass equilibrated with Ak30 Mel and Ak80 Mel is only 0.5. Analyses (10) of 14 Mel-Fass pairs were chosen from one Type B2 and three Type B1 inclusions specifically because of textural evidence for co-crystallization of the analyzed grains. Because Sp is present throughout the crystallization sequence of Type B inclusion compositions (11), we assumed that each Mel-Fass pair equilibrated with Sp. Log f_{O_2} values calculated at 1500K were averaged for reactions A and B for each Mel-Fass pair and plotted vs wt% Ti_2O_3 in Fass in Fig. 1. Also shown are log f_{O_2}'s for a solar gas and the NNO, QFM and WI buffers. The error bars incorporate analytical, thermochemical and calibration errors as well as possible errors in assumed T. For Fass with > 3 wt% Ti_2O_3, the average log f_{O_2} for all analyzed pairs is $-19.5\pm.7$. This is at least as reducing and possibly much more reducing than a solar gas whose log f_{O_2} is ($-18.1\pm.4$) at 1500K, corresponding to an atomic C/O ratio of .56±.14. It is 8 orders of magnitude more reducing than WI and corresponds to a nebular C/O of .85±.06. There is no discernible difference in calculated log f_{O_2} between B1's and B2's, implying that both inclusion types could have equilibrated with the same gas. In a given inclusion, calculated f_{O_2}'s are different for pairs containing Fass with < 3wt% Ti_2O_3 and Fass with > 3 wt% Ti_2O_3 For TS-23, the pair contains Fass with the lowest Ti_2O_3 yields a slightly lower f_{O_2} than other pairs. Calculated f_{O_2}'s from TS-34 and TS-47 are constant for Fass with > 3 wt% Ti_2O_3 and increase by a factor of more than 100 as Ti_2O_3 decreases in Fass with <3 wt% Ti_2O_3. Similarly, constant f_{O_2} for Ti_2O_3-rich Fass and progressively higher f_{O_2}'s with decreasing Ti_2O_3 in Ti_2O_3-poor Fass were observed on a traverse across an individual Fass grain in TS-34 and across several grains in TS-20. The higher f_{O_2}'s calculated for Ti_2O_3-poor Fass may be due to errors in the solution model for Fass and/or analytical errors. Alternatively, the higher f_{O_2}'s could be real. Since Ti_2O_3 generally decreases from core to rim in Fass (6), pairs containing low-Ti_2O_3 Fass may have crystallized at lower temperatures than those containing high-Ti_2O_3 Fass. Possibly, late stage Fass growth occurred in a more oxidizing gas than earlier Fass. Fass-Mel pairs have not been analyzed in Type A inclusions. Using published Fass analyses (5,12) and ranges of X_{Ak} for 3 inclusions leads to calculated log f_{O_2} = $-17.8\pm.3$. This is within error of the f_{O_2} for a solar gas. Thus, A's, may have equilibrated in a slightly more oxidizing gas than Type B's.

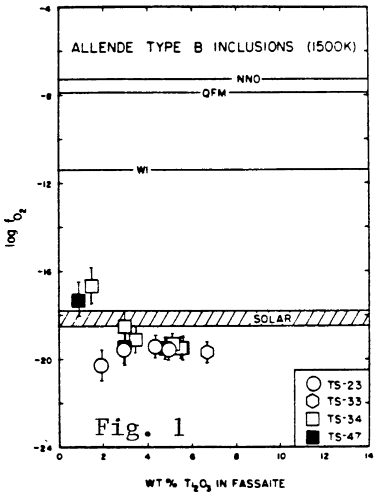

Fig. 1

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