

## Diffusion and solubility of C in Pt

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### ABSTRACT

Diffusion experiments using  $^{14}\text{C}$  as a radiotracer reveal that reduced C is slightly soluble in polycrystalline Pt at 1.5 GPa ( $\sim 10\text{--}280$  ppm atomic over the temperature range  $1200\text{--}1500^\circ\text{C}$ ) and also has a high diffusivity ( $\sim 10^{-5}$   $\text{cm}^2/\text{s}$ ). The combination of these two characteristics results in a significant permeability of Pt to C, which under some circumstances can affect the abundance of C-bearing species in an experimental capsule.

### INTRODUCTION

As a commonly employed container for high-pressure and high-temperature experimentation on rock and mineral materials, Pt is frequently used to encapsulate C-bearing fluids and melts. Knowledge of the compositions of such fluids is generally predicated on the assumption that a properly welded Pt capsule is impermeable to all C species present. Recently, however, experiments involving confinement of  $\text{CO}_2$  in Pt showed that this assumption is not always correct (Watson et al., 1982, p. 348) and that (presumably reduced) C can diffuse through the container walls. These conclusions were later substantiated by Fine and Stolper (1985), who noted that the total dissolved carbonate content of a Pt-encapsulated silicate melt decreases as a function of duration at elevated  $P$ - $T$  conditions in a piston-cylinder apparatus. Again, this observation seemed to suggest that small amounts of carbonate in the experimental materials were reduced to elemental C, which subsequently dissolved in the Pt and diffused outward through the container walls.

In view of the effects described above, and because of the importance of maintaining constant amounts of C-bearing species within an experimental capsule, the solubility and diffusivity of reduced C in Pt was studied. The intent was to develop some guidelines for predicting C loss from Pt containers run in a piston-cylinder apparatus. The specific data required for such a prediction include the solubility and diffusivity of C in Pt at representative  $P$ - $T$  conditions.

### TECHNIQUES

The published phase diagram for the Pt-C system at 1 atm indicates rather low solubilities of C in Pt—i.e., 2–4 at.% at most, this occurring just below the binary eutectic at  $1705^\circ\text{C}$  (Moffat, 1984). For this reason, it seemed inappropriate to undertake analysis of experimental C-diffusion profiles with the electron microprobe. I resorted instead to a technique using  $^{14}\text{C}$  as a radiotracer, purchased from Dupont NEN as amorphous C and diluted by thorough mixing with finely powdered graphite. Any C present in Pt could thus be readily detected by beta-

track autoradiography (e.g., Mysen and Seitz, 1975; Tingle, 1987).

Diffusion experiments were performed on Pt cylinders 2 mm in diameter by  $\sim 4$  mm long, which were annealed at yellow heat ( $\sim 1200\text{--}1300^\circ\text{C}$ ) for about 10 min prior to use. The cylinders were fitted into fired crushable alumina sleeves, and a bottom piece of the same material was inserted into one end of the sleeve. Before inserting a similar plug at the other end,  $\sim 0.5$  mg ( $\sim 0.01$   $\mu\text{Ci}$ ) of the  $^{14}\text{C}$ -doped graphite powder was deposited on the polished surface of the Pt cylinder. The  $\text{Al}_2\text{O}_3$ -encased cylinder with  $^{14}\text{C}$  source at one end was then placed in a 0.5-in. piston-cylinder assembly consisting of Pyrex and crushable  $\text{Al}_2\text{O}_3$  inner pieces and an outer sleeve of NaCl (see Fig. 1). The intrinsic oxygen fugacity of this assembly is known to be just below the fayalite-magnetite-quartz equilibrium.

An experiment was initiated by cold pressurization of the Pt cylinder to 1.5 GPa (15 kbar), followed by rapid heating to a prescribed temperature in the range  $1100\text{--}1500^\circ\text{C}$ . The pressure was continuously adjusted during the 30-s heat-up period to maintain a value close to the desired 1.5 GPa. The experiments were terminated by turning off the power to the furnace, which resulted in a cooling rate of about 200 deg/s. A summary of information on experiment conditions and durations is provided in Table 1.

The Pt cylinders were recovered by breaking away the surrounding alumina sleeve and were mounted in epoxy for sectioning along the cylinder axis and subsequent polishing of the sectioned surface with 1- $\mu\text{m}$  grit. The polished samples were then placed against Ilford type K5 nuclear-emulsion plates to record the 0.156-MeV beta particles emitted by  $^{14}\text{C}$  dissolved in the Pt. Because of the generally small amounts of C present, exposure times of up to 480 h were required to produce meaningful beta-track maps.

Information on C concentration and transport distance was extracted from microdensitometer traverses of the developed nuclear emulsions, which were made with a  $\sim 10\text{-}$  by 1000- $\mu\text{m}$  scanning slit. Diffusivities were cal-

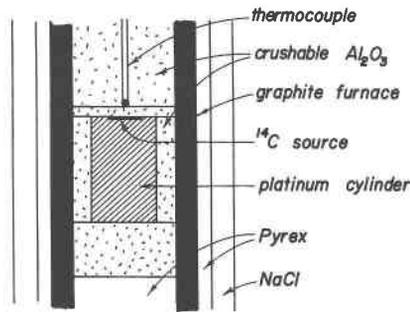


Fig. 1. Arrangement of Pt cylinder and  $^{14}\text{C}$  source in the piston-cylinder assembly.

culated by fitting the densitometer scans to the solution of Fick's second law for one-dimensional diffusion into a semi-infinite medium from a surface held at constant concentration (Crank, 1975):

$$C_x/C_0 = 1 - \text{erf}[x/(4Dt)^{1/2}]$$

where  $D$  is the diffusivity ( $\text{cm}^2/\text{s}$ ),  $t$  is time, and  $C_x$  is the concentration at some distance  $x$  from the surface (at  $x = 0$ ) where the concentration is  $C_0$ . The light-absorbance values recorded by the densitometer are proportional to the beta-track density on the nuclear-emulsion plate, which in turn is proportional to the concentration of  $^{14}\text{C}$  in the Pt sample to which the plate was exposed. The fits to the densitometer scans were performed by the method described in Harrison and Watson (1983), which returns not only a diffusivity (with estimated uncertainty), but also the value of  $C_0$ , which is proportional to the surface concentration of C in the Pt. (In all cases, the correlation coefficients for the fits to the linearized diffusion profiles were 0.994 or higher.) The  $C_0$  values were converted to absolute concentrations by comparison with the track density resulting from exposure of a nuclear-emulsion plate to the  $^{14}\text{C}$ -doped source material. In computing the concentrations, a correction was made for the  $\sim 4$ -fold difference between the range of 0.156 MeV beta particles in Pt and that in graphite (see Tingle, 1987), but no attempt was made to account for latent track fading that

must have occurred in the long exposures necessitated by the low concentrations of C in the Pt (Jones and Burnett, 1981; Tingle, 1987). Because the exposure of the  $^{14}\text{C}$  source was very brief by comparison (thus resulting in little or no latent track fading), the computed concentrations are *minimum* values and may be low by as much as a factor of two.

The fact that the source of  $^{14}\text{C}$  is pure C means that the final surface concentrations in the Pt cylinders represent solubilities of C in Pt at the experimental conditions (1100–1500°C, 1.5 GPa).

## RESULTS

The results of seven experiments are shown as photographs of beta-track maps in Figure 2. Computed values for C diffusivity and solubility are included in Table 1 and are summarized in Figures 3 and 4.

The first two experiments (1100 and 1300°C) showed on the one hand that the solubility of C in Pt is low (in fact, below detectability at 1100°C) but strongly temperature-dependent. The diffusivity, on the other hand, is so high that a uniform concentration of C in Pt is achieved in less than 2 h at 1300°C (see Fig. 2). The early experiments also revealed that there is some tendency for C to diffuse along the *surface* of the Pt cylinder rather than through it; this complication is of little importance because the two transport paths are readily distinguished on the beta-track maps.

As shown in Figures 3 and 4, the last five experiments reveal a systematic dependence of both diffusivity and solubility upon reciprocal absolute temperature. The Arrhenius equation for diffusion is given by

$$D_c = 0.017 \exp(-25\,000/RT),$$

where the activation energy of 25 kcal/mol (104.6 kJ/mol) has a 2-sigma uncertainty of  $\sim 25\%$ . The solubility of C in Pt is given by

$$\ln C = -29\,350/T + 22.4.$$

This equation describes solubilities markedly lower than those implied by published Pt-C phase diagrams (Moffat,

TABLE 1. Summary of experiment conditions and data

Run	$T$ (°C)	Experiment time (s)	Exposure time* (h)	C solubility** (ppm atomic)	C diffusivity ( $\text{cm}^2/\text{s}$ )	Comments
1	1000	1800	681	—	—	Below detection†
2	1300	7200	173	60	—	Experiment too long‡
3	1300	900	173	50	$6.1 \times 10^{-6}$	
3	1300	900	478	50	$5.5 \times 10^{-6}$	
4	1200	3600	478	10	—	Experiment too long‡
5	1400	180	173	140	$9.7 \times 10^{-6}$	
6	1200	1200	478	10	$2.8 \times 10^{-6}$	
7	1500	180	173	280	$1.1 \times 10^{-5}$	

\* Exposure time of nuclear-emulsion plate to sample.

\*\* These values are minima and may be low by as much as a factor of two (see text).

† No beta tracks observed in Pt.

‡ Because of long experiment duration, the Pt cylinder was noninfinite with respect to C diffusion.

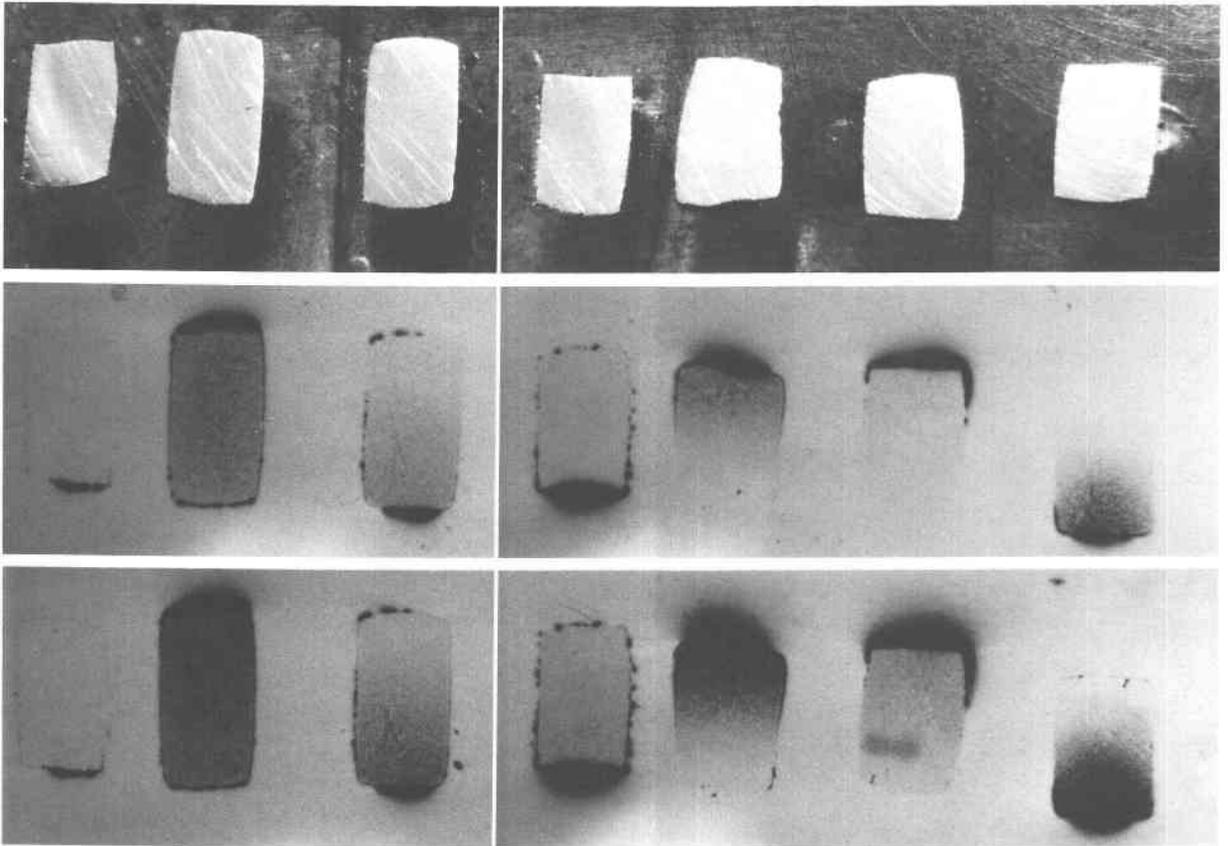


Fig. 2. Sectioned Pt cylinders from experiments 1-7 (top row, left to right) and corresponding beta-track maps produced by exposures of 173 h (middle row) and 478 h (bottom row). The cylinders are 3-5 mm long. See text for discussion.

1984), but the discrepancy is reasonably attributed to the 1.5-GPa difference in pressure between experiments of this study and the 1-atm phase relations.

A final detail concerning the experimental results is that the beta-track maps reveal a distribution of C on a local scale that is distinctly nonuniform. This is clearly shown in Figure 5, a high-magnification photograph of the beta-track map from run 3. The resolution of the mapping technique is not sufficiently good to conclude unequivocally that C is concentrated along grain boundaries in the Pt, but this is certainly suggested by the local heterogeneity in C distribution. There is no indication from reflected-light microscopy that graphite forms a second phase. If C atoms are located primarily at grain boundaries, then the solubility and diffusivity measurements of this study must be regarded as bulk values for polycrystalline Pt and are not relevant to single crystals. Although it is important that this distinction be made, it should also be noted that the Pt tubing used in experimental studies is polycrystalline, so the present data are relevant to the problem at hand. The apparent enrichment of C along grain boundaries implies, of course, that the bulk solubility and diffusivity will depend somewhat upon grain size.

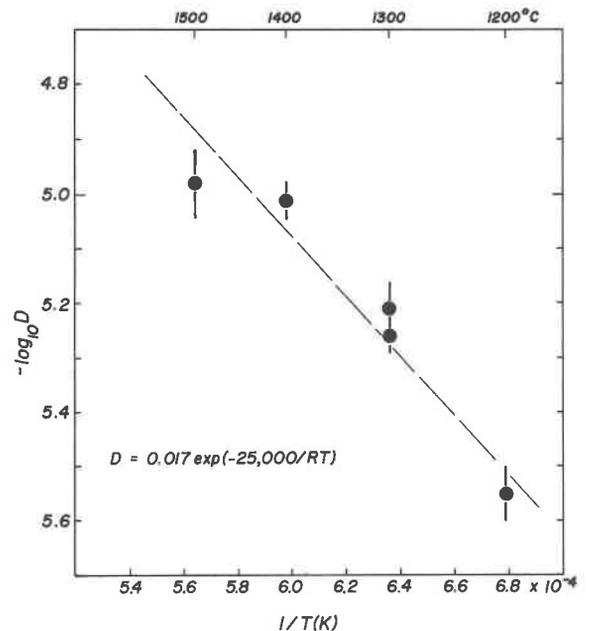


Fig. 3. Arrhenius diagram of C diffusion data. The equation for the least-squares fit is given in the figure, with  $R$  in cal/deg-mol. The activation energy of 25 kcal/mol has a 2-sigma uncertainty of  $\pm 25\%$ .

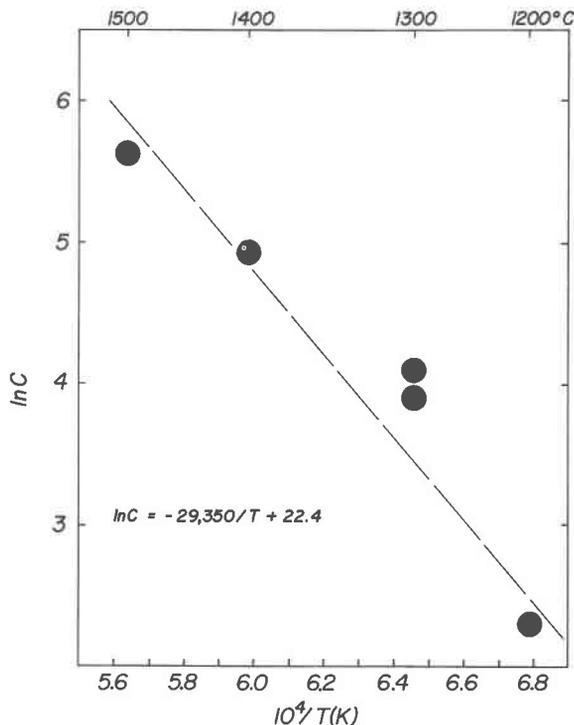


Fig. 4. Summary of C solubility measurements illustrating systematic temperature dependence. As discussed in the text, these solubilities are considered to be minimum values (because of latent beta-track fading in the nuclear emulsions); they pertain to polycrystalline Pt.

### IMPLICATIONS

The experimental results confirm that C loss from a Pt container can occur and under some circumstances could be extremely rapid. This possibility arises in spite of the fact that the solubility of C in Pt at high pressure is low and is due specifically to a very high diffusivity. (The parameter of real interest is the permeability of Pt to C, which is given by the product of the diffusivity and the solubility.) In any given experiment, the severity of the problem will depend upon a number of factors, the most important of which may be oxidation-reduction reactions within the Pt capsule. Presumably, Pt is permeable to elemental C only, so some mechanism—perhaps inward diffusion of H (Fine and Stolper, 1985)—must operate to reduce carbonate species present in the contained fluid or melt.

Another important factor may be the gradient in C activity across the wall of the Pt capsule. If the capsule itself were surrounded by graphite, there would be no “driving force” for outward flux of C (in fact, C might diffuse *into* the contained sample).

In the final analysis, the possibility of C loss (or gain) must be examined in the context of the specific experimental arrangement employed. Given knowledge of C concentration both within and outside a Pt container, the flux ( $J$ ) through the container wall could be computed from the steady-state diffusion equation,  $J = -D(\Delta c/\Delta x)$ ,

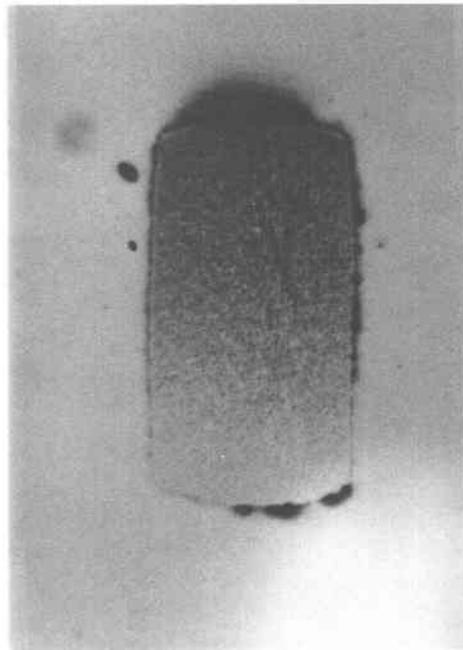


Fig. 5. Beta-track map of the Pt cylinder from run no. 3, illustrating the nonuniform distribution of C. This heterogeneity is probably due to preferred concentration of C at Pt grain boundaries.

where  $\Delta c$  is the concentration difference across a capsule wall of thickness  $\Delta x$ . In several types of experiments, all involving  $\text{CO}_2$  as a free fluid phase, nontrivial effects of C diffusion in Pt have been observed.

### ACKNOWLEDGMENTS

The manuscript benefitted from discussions with W. A. Lanford on the subject of beta-particle ranges. This work and many of the experiments leading to it were supported by the Earth Sciences Division of the National Science Foundation, under Grant EAR84-06200.

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MANUSCRIPT RECEIVED AUGUST 26, 1986

MANUSCRIPT ACCEPTED FEBRUARY 2, 1987