STUDIES ON THE ROLE OF \( \text{CO}_2 \) AND \( \text{CO} \) IN MAGMA GENESIS IN PLANETARY INTERIORS. David H. Eggler, Department of Geosciences, The Pennsylvania State University, University Park, Pa. 16802

Experimental and theoretical studies have been conducted on gases in the system \( \text{C}-\text{O} \), particularly in equilibrium with graphite, and on the solubility of \( \text{C}-\text{O} \) gases in silicate melts.

1. Composition of gases in the system \( \text{C}-\text{O} \), in equilibrium with graphite.
   Direct analysis of gases quenched from high pressures and temperatures has proved feasible, but results suggest that gases have reequilibrated during the quench, producing mixtures of \( \text{CO}_2 \) and \( \text{CO} \) more \( \text{CO}_2 \)-rich than the compositions at high \( \text{P-T} \) conditions. Calculations using modified Redlich-Kwong thermodynamic functions (1) indicate that \( \text{CO} \)-rich gases are not to be expected except at pressures less than about 10 kbar and temperatures in excess of about 1300°C.

2. Solubilities of \( \text{CO}_2 \) and \( \text{CO} \) in silicate melts. Techniques have been developed for generation of \( \text{CO} \) gas and graphite with uniform C content in order to analyze the C content of glasses quenched from high \( \text{P-T} \) conditions by autoradiography. The most successful reactant is fumaric acid; \( \text{H}_2 \) is allowed to escape from capsules in an argon-pressurized vessel equipped with a hydrogen (Shaw) membrane. Solubilities of \( \text{CO} \) in synthetic silicate compositions, principally diopside, at pressures above about 15 kbar and at liquidus temperatures are as large or larger than solubilities of \( \text{CO}_2 \); solubilities of \( \text{CO}_2-\text{CO} \) gas (in equilibrium with graphite) and of \( \text{CO}_2 \) gas in diopside melt at its liquidus at 20 kbar are about 2.5 wt percent (C as \( \text{CO}_2 \)). At superliquidus temperatures, however, \( \text{CO}_2 \) is more soluble than \( \text{CO}-\text{CO}_2 \).
   Preliminary results on solubilities of \( \text{C}-\text{O} \) gases in mare basaltic melts at pressures of 2-20 kbar suggest that solubilities are not very different from solubilities in terrestrial basalts (2) — e.g., about 1 percent \( \text{CO}_2 \) or \( \text{CO}-\text{CO}_2 \) at 5 kbar pressure. The \( \text{CO}-\text{CO}_2 \) solubilities are more applicable to lunar petrogenesis than the \( \text{CO}_2 \) solubilities. The relative magnitude of the solubilities opens the possibilities that outgassing could have occurred during basaltic volcanism and that boiling of \( \text{CO}-\text{CO}_2 \) gas could account for some lunar pyroclastic activity.

3. The enstatite-magnesite-olivine-graphite (EMOG) \( f_0^2 \) buffer. Experiments at high pressures and temperatures have confirmed (2) that the assemblage enstatite-magnesite-olivine-graphite is to be expected in any planetary interior that contains olivine, pyroxenes, and graphite, provided that \( \text{P-T} \) conditions are within its stability field (temperatures below a line passing through the approximate coordinates 800°C/10 kbar, 1000°C/20 kbar, 1400°C/40 kbar). The EMOG assemblage is an oxygen buffer:

\[
\text{MgSiO}_3 + \text{MgCu}_3 = \text{Mg}_2\text{SiO}_4 + \text{C} + \text{O}_2
\]

En Mag Oliv graph

This buffer should be the principal control on \( f_0^2 \) in planetary interiors that contain olivine, pyroxenes, and graphite and that lack other \( f_0^2 \). This situation is considered to be "normal". By example, if iron \( \text{O}_2 \) exists essentially entirely as \( \text{FeO} \), iron-bearing minerals have no oxygen buffer capacity. The EMOG buffer will operate whether or not other gas species are present. At temperatures in excess of the stability of the EMOG assemblage, the \( \text{CCO} \) buffer (3) applies, but only if \( \text{CO} \) and \( \text{CO}_2 \) are the only gas species present in the planetary interior.
Attempts to calibrate the EMOG buffer experimentally have thus far been unsuccessful, primarily because the assemblage lacks a gas phase that could equilibrate with a "test buffer" at high $P$ and $T$. Indirect methods are being pursued. The reaction can be calculated, however, from free energy data on the reaction $En + Mag = Fo + CO_2$ (4) and 1-bar gas data and molar volumes from (5):

$$\log f_{O_2} = 8.93 - \frac{25295}{T} + \frac{0.045(P-1)(K, \text{bar})}{T}$$

Oxygen fugacities of the EMOG buffer, between 10 kbar and 50 kbar, range between the QFM and WM buffers, decreasing (isothermally) with depth.

References