THEORETICAL ASPECTS OF GASEOUS AND ISOTOPIC EQUILIBRIA IN THE SYSTEM C-H-O-S WITH APPLICATION TO KIMBERLITES

Roger H. Mitchell

Dept.of Geology, Lakehead University, Thunder Bay, Ont, Canada.

Real gas equilibria are evaluated by assuming that continuous equilibrium is established between graphite or diamond and a gas phase whose composition lies within the system C-H-O-S.It is further assumed that $CO_2, CO, CH_4, H_2O, H_2S, H_2$ and SO₂ are the major species formed and that formation of hydrocarbons more complex than CH_4 is limited.Following the methods of French(1966) the partial pressure(P_i) of any species at any T and P can be calculated if fo₂, fs₂, fugacity coefficients and equilibrium constants are known for the following reactions:-

(1) $C + O_2 = CO_2$; (2) $C + \frac{1}{2}O_2 = CO$; (3) $C + 2H_2 = CH_4$ (4) $H_2 + \frac{1}{2}O_2 = H_2O$; (5) $\frac{1}{2}S_2 + O_2 = SO_2$; (6) $\frac{1}{2}S_2 + H_2 = H_2S$ Thus if fo_2 and fs_2 for a given magma can be determined from the mineral assemblages present it is possible to calculate the composition of the gas phase in equilibrium with that magma if it contains carbon as graphite or diamond. Gas equilibria are discussed here for the rapid expansion phase of kimberlite emplacement from high pressures (2-10 kbs) to low pressure (1 kb) over the temperature range $800-600^{\circ}C.,i.e.$ essentially during the time of formation of the groundmass.

Oxygen fugacities are calculated for the groundmass assemblage olivine+magnetite+liquid by the quartz-fayalitemagnetite buffer.Silica activities for this buffer are defined by the akermanite-forsterite-diopside buffer (Mitchell 1973).Sulfur fugacities are estimated to be on the order of 10⁻⁵ bars(coexisting magnetite and pyrite) but calculations are extended to cover a wide range in fs₂.

During the last stages of kimberlite emplacement it is considered that P variation is more important than T variation, overpressures being responsible for the fluidized gas drive.Figure 1 shows the calculated composition of the gas phase up to 10 kbs., over a T range of 200°K. Prefluidized conditions in pools of kimberlite magma in the lower crust are considered to be within the 1000-1100°K, 4-10 kb., portion of the diagram. The most important conclusions to be drawn from the calculations are that over much of the PT range H_2O is the dominant gas and that the proportions of CH_A to CO2 can vary widely, falling P at constant T promoting an increase in CO2 content. The dominant phases during fluidized intrusion are H_2O, CO_2 and CH_4 . As P falls to the post fluidized conditions of the groundmass it can be seen that CH₄ still makes up a considerable percentage of the fluid phase, however low pressures favour a fluid phase composed essentially of H₂O and CO₂, this conclusion being in accord with the extensive serpentinization and hydration of primary minerals and the formation of late stage carbonates.Under all conditions of fs_2 , P_{H_2S} is very much greater than P_{SO_2} and H_2S becomes the dominant gas in the C-H-O-S system when fs_2 reaches 10° bars. SO_2 is at all times a minor component.The presence of abundant CH₄ in the fluid phase is in agreement with Kogarko's(1972) calculated fluid phase composition of agpaiitic syenites(Table 1) at low pressures.Coexistance of high partial pressures of CH₄ and CO₂ would thus seem to be a feature of both sodic and potassic alkaline rocks.

Table	1.0	Comparison	of	gas	composit:	ions	of	ki	mbe	erlite	a	nd
Lovoze	ero	nepheline	SVe	enite	(Kogarko	1972) a	it.	l k	b.		

	C-H-O-S Log.partial pressure						
Gas	Kimberlite	Syenite					
$\begin{array}{c} \text{CO}_2\\ \text{CO}\\ \text{CH}_4\\ \text{H}_2\text{O}\\ \text{H}_2\\ \text{H}_2\text{S}\\ \text{SO}_2\\ \text{fo}_2\\ \text{fs}_2 \end{array}$	2.48 0.74 1.89 2.76 1.17 1.41 -5.69 -20.38 -5.0	1.91 -0.21 2.50 2.52 1.15 2.78 -5.76 -23.79 -3.75					
тС	627	525					

Isotopic studies have shown that diamonds are not of uniform isotopic composition i.e.world wide variation in Σ^{13} C is from -1.9 % oo to - 9.7 % oo with up to 3 % oo variation being found in a single pipe (Vinogradov and Kropotova 1967). The natural isotopic variations require that diamonds form in an environment where isotopic fractionation can occur. Deep in the mantle at high P and T fractionation should be negligble. Mitchell and Crocket(1971) have proposed that some diamonds can form metastably by gas reduction mechanisms in the lower crust, the diamond growing on diamond seed nuclei prior to fluidized intrusion. Under these conditions carbon isotopic fractionation between carbon bearing gases is appreciable e.g. at 1000°K the isotopic composition of CH₄ and CO₂ differ by 10 % oo. For solid phases i.e. graphite or diamond forming by gas reduction from carbon bearing gaseous species one can write:-

$$S^{13}C_{\text{graphite}} = S^{13}_{\text{Czc}} - \left[(\Delta \text{Co}_2 \cdot \text{x Co}_2) + (\Delta \text{Co} \cdot \text{x Co}) + (\Delta \text{Ch}_4 \cdot \text{x Ch}_4) \right]$$
(7)

$$\varsigma^{13}C_{\text{diamond}} = \varsigma^{13}C_{\text{graphite}} + \Delta_{\text{diamond}}$$

where $\delta^{13}C_{\text{LC}}$ is the mean isotopic composition of the fluid phase, Δ_i and X_i are the relative isotopic enrichment factors between species i and graphite and the mole fraction of the species in the gas phase respectively (Ohmoto 1972).

Substitution of the data from figure 1 into equations (7) and (8) gives the change in isotopic composition of graphite or diamond with changing composition of the fluid phase in response to variations in P,T,fo2,fs2. The calculations show that at 1000° K and 5-10 kb a 6 0/00 change in the isotopic composition of the reduced solid phase can occur. This change is largely in response to variation in the CH4/CO2 ratio of the parent gases. The calculated isotopic variations can thus account for the observed variation in isotopic composition of diamond and predicts that extensive variation will be found in the isotopic composition of kimberlitic graphites. A problem with the hypothesis is that it is unknown whether a metastable phase (diamond) can exist in isotopic equilibrium with the material from which it formed.If isotopic equilibrium is not allowed the spread in the isotopic composition of diamond must be due to nonequilibrium kinetic isotope effects. The hypothesis also assumes that the amount of carbon present as a solid phase is small compared to the amount present in the gas phase.

References

French,B.W.1966. Revs.Geophys.4,223-253. Kogarko,L.N.,1972. Proc.24th.Internat.Geol.Cong.v.10,20-24. Mitchell,R.H.1973. Lithos,6,65-81. Mitchell,R.H., and Crocket,J.H.1971.Mineral.Deposita 6,392-403 Ohmoto,H.1972.Econ.Geol.67,551-578. Vinogradov,A.P., and Kropotova,O.I.1967.Internat.Geol.Rev., 10,497-506.

