SYNTHESIS OF C-H-O FLUIDS AT HIGH PRESSURE.

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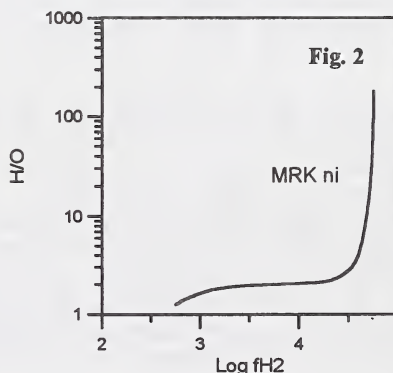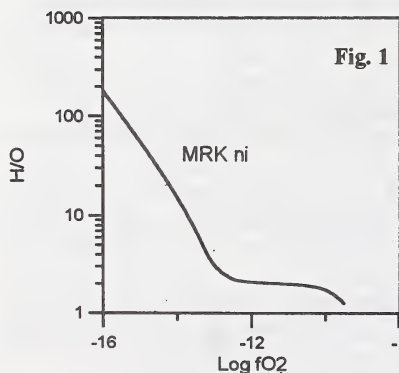
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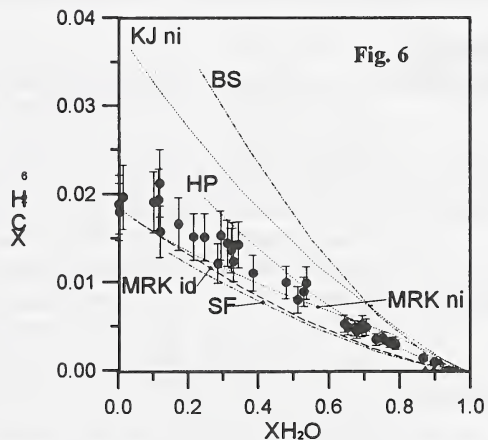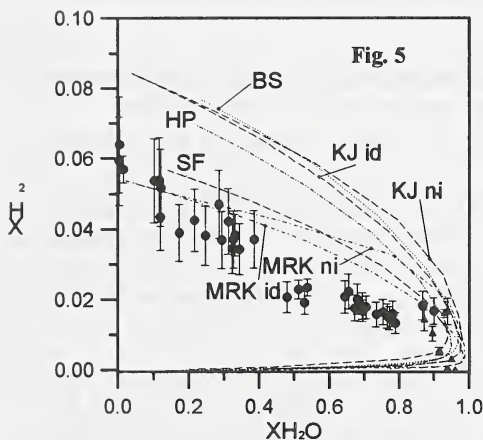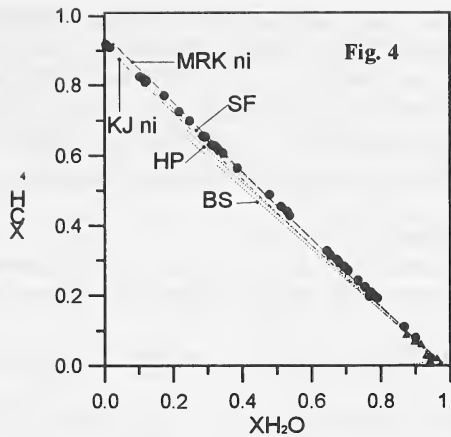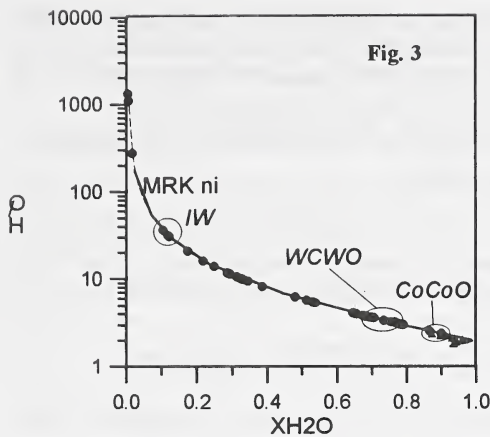4. Institute for Geology of Ore Deposits, 35 Staromonetny Per., Moscow 109017, Russia.

C-H-O fluids play an important role in igneous processes. They determine the P, T position of the mantle solidus (Taylor and Green 1988) and influence seismic properties. They are also the principal carriers for carbon in the mantle and thus can be relevant for diamond formation. Fluid speciations may be calculated using numerous equations of state (EoS), although at high P these EoS, and especially the assumption that molecules behave as hard spheres, become increasingly uncertain. Thus, in an affort to revise existing EoS and extend them to high P, we have synthesized CHO fluids in equilibrium with graphite at 1000°C and 2.4 Gpa. Our H/O bulk fluid ratios ranged from 1.79 to about 1330.

Experiments were carried out in a piston-cylinder apparatus. Talc outer sleeves and boron nitride crucibles were used to impose high hydrogen and low oxygen fugacities around the capsule, ie. to minimize hydrogen loss during experiment. Capsule materials are Pt for relatively oxidized conditions (H/O around 2) and Au for reduced conditions (H/O > 3). CHO starting materials are water, stearic acid ($C_{18}H_{36}O_2$), benzoic acid ($C_6H_5*CO_2H$) and graphite. In some experiments fluids were internally buffered by metal-oxide buffers (SiC-SiO2, IW, W-C-WO2, CoCoO). Run times ranged from 0,5 h for highly reduced conditions (IW), to 48h for experiments near the water maximum (H/O ~ 2). H_2O, CO_2, CO, CH_4, C_2H_6 and H_2 in the fluids were analyzed by gas chromatography (Ziegenbein and Johannes 1977). Precision of analysis were better than 12% relative for minor species, and 6% relative for major species. Typical fluid compositions are presented in Table 1.

Table 1: **Typical fluid compositions at 1000°C and 2.4 Gpa (mole percent)**

fO2 range	CO_2	CH_4	C_2H_6	H_2	H_2O	H/O
H_2O-CO_2	6.2	0.3	0	0	93.5	1.78
H_2O max	2.2	2.3	0	0.3	95.0	2.00
H_2O-CH_4	0	22.6	0.4	1.6	75.3	3.26
CH_4-H_2-H_2O	0	65.4	1.5	3.7	29.3	11.5
Fe-FeO	0	81.0	1.9	5.4	11.7	31.7
SiC-SiO2-C	0	91.9	1.9	5.9	0.3	1330

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Experiments in ● gold capsules; ▲ platinum capsules. Error bars indicate double absolute deviation of analysis.

The obtained data were compared with the following equations of state:

1) ideal mixing models: *a)* **MRK id** - Holloway (1977, 1981), where a(T) is a third order polynom for CO_2 and H_2O; the b and a parameters for hydrogen are from Holloway (1981) and the b and a parameters for C_2H_6 were recalculated from Redlich and Kwong (1949); *b)* **HP** - compensated RK by Holland and Powell (1991); *c)* **SF** - Saxena and Fei (1987) EoS with γ for H_2 obtained from Belonoshko and Saxena (1992); *d)* **BS** - Belonoshko and Saxena (1992), with recalculations for ethane from Saxena and Fei (1987); *e)* **KJ id** - Kerrick and Jacobs (1981) model for CO_2,H_2O, with Jacobs and Kerrick (1981) for CH_4. Fugacities for other species were recalculated after Holland and Powell (1991).

2) non-ideal mixing for major species (CH_4 and H_2O):

a) **MRK ni** - MRK (Holloway, 1977) with Flowers' (1979) corrections;

b) **KJ ni** - Kerrick and Jacobs (1981); Jacobs and Kerrick (1981).

The results are illustrated in Fig. 1 to 6. Values for fO_2 and fH_2 are calculated from H/O bulk fluid ratios (Fig.1 and 2) using *MRK ni*.. Fig.3 shows the variation of H_2O with the H/O bulk ratio, with points of the buffered exteriments marked on the curve. All EoS predict nearly the same relationship, so we only superimpose the curve recalculated from *MRK ni*. The correlation of CH_4 and H_2O concentrations in the fluid is shown on Fig.4. The good agreement with theoretical models is no surprise since H_2O and CH_4 are the principal components of

the fluid. Fig.5 illustrates the hydrogen content of the fluid, and Fig.6 the C_2H_6 content, both as functions of XH_2O. Hydrogen content is slightly lower than predicted by any theoretical model, especially in the range of intermediate water contents (fO_2 around WCWO), while C_2H_6 behaves as predicted from most MRK equations. The internal consistency of our experimental results, in particular with respect to hydrogen and ethane, suggests that chemical equilibrium reached and that quenching effects are negligible.

Preliminary conclusions:
1) The best fit to our experimental fluid compositions is provided by the relatively simple EoS such as the *MRK id* and *MRK ni*. More complex models do not seem to be warranted.

2) CHO fluids are easily quenchable from high P and T in piston-cylinder apparatuses.

3) Our experimental setup, i.e. gold capsules contained in boron nitride and surrounded by talc sleeves, allows reliable control of hydrogen fugacity during high pressure experiments.

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