

Cobaltous oxide as a chemical analogue for ferrous iron in experimental petrology: an alternative solution to the iron-loss problem

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Abstract

The loss of iron from starting compositions to noble-metal capsule materials is a serious experimental problem which occurs at high temperature over the most interesting ranges of oxygen fugacity. One-atmosphere experiments indicate that equimolar substitution of CoO for FeO creates an analogue system which maintains constant composition, enabling equilibrium experiments to be performed. Using CoO as a chemical substitute for FeO permits the experimenter to simulate any desired oxygen fugacity, accurately reproduce phase relations occurring in ferromagnesian systems, and generate liquid compositions which may be corrected to yield accurate estimations of FeO-bearing liquids. To a lesser degree, temperatures may also be corrected. Available data indicate that the analogue remains valid at high pressure. Thus, the cobalt analogue technique provides a flexible alternative for modelling mafic systems at high temperature while avoiding the 'iron-loss problem.'

Introduction

During the past two decades the number of experiments conducted on ferromagnesian rock compositions has risen dramatically. The development of new techniques and apparatus, which attain temperatures of 1700°C and pressures of 35 kbar routinely, is largely responsible. The ability to reproduce upper mantle–lower crust conditions has led to considerable experimentation on peridotite and other 'basaltic' compositions. However, these experiments have been plagued by a persistent experimental problem—iron loss.

The iron-loss problem

Simply stated, the 'iron-loss problem' results when the iron content of the sample at the end of an experiment is lower than it is in the starting composition. This phenomenon arises at high temperature, over the most interesting oxygen fugacity ranges, and is

due to the considerable solubility of iron in the more popular capsule materials. In a typical piston cylinder experiment, at temperatures in excess of 1200°C, it has been demonstrated that the relative loss of FeO to a platinum capsule from an andesite composition is nearly 100 percent in 3 hours (Stern and Wyllie, 1975). While iron loss is not always as severe as this, varying as a function of capsule material and temperature, it is an inescapable fact that equilibrium experiments cannot be conducted when the bulk composition is changing.

There have been many attempts to curb or eliminate iron loss, some more successful than others. The best method is to reduce relative loss by maximizing the sample/capsule mass ratio (*e.g.* Hill, 1969; Holloway and Burnham, 1972; Helz, 1973). While this method is generally applicable to one-atm experiments (and can be used up to 10 kbar with a large-volume, gas-media pressure vessel), it is impossible to maintain a large sample/capsule ratio during piston cylinder experiments because of the small samples, about 10 milligrams.

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Other capsule materials such as graphite, molybdenum, and iron have been used to alleviate iron loss. However, none of these materials may be used with confidence to contain experiments in which the prevailing oxygen fugacity significantly exceeds that defined by the reaction: $\text{Fe} + \frac{1}{2}\text{O}_2 = \text{FeO}$ (Walker *et al.*, 1972). In addition none of these materials is strictly inert. In the presence of a vapor, graphite dissolves iron, and cannot be exposed to water without producing additional species such as CO_2 and CH_4 . Molybdenum also dissolves some iron, and a system devoid of TiO_2 must be used or the capsule will react to form MoTiO_4 and ultimately fail (Biggar, 1970). Iron capsules should only be used in systems precisely saturated with Fe, otherwise a chemical potential gradient exists, which causes iron to be added to or subtracted from the starting composition in order to reach the saturation value (Kesson, 1974).

The remaining capsule materials in common usage are noble metals and their alloys. These metals allow experiments to be conducted over wide ranges of oxygen fugacity, and so are the most widely used. Neither gold nor silver dissolves iron in appreciable amounts. However, their relatively low melting points (at one atmosphere 1063° and 910°C, respectively) preclude their use in high-temperature experiments. Platinum and alloys of silver and palladium are thus the materials of choice when conducting most high-temperature experiments. However, iron loss to these materials may be considerable (Stern and Wyllie, 1975).

It has been proposed that experiment duration be kept to a minimum (*e.g.* Wyllie and co-workers; Green and co-workers) to minimize Fe loss. However, contrary to alleviating the problem, this procedure compounds the error. Stern and Wyllie (1975) have shown that up to 40 percent of the FeO in an andesite may be lost to platinum in as little as 20 minutes. Thus, because most of the iron loss occurs early in the experiment, conducting experiments of short duration serves only to compromise equilibrium.

Earlier, Holloway (written communication to Wyllie, 1974) advocated finding a new capsule material or confining experiments to iron-free systems. The first suggestion has strong appeal but is subject to the discovery of a presently unknown material. The second has been applied by Muan and co-workers, who used iron-free systems to model natural compositions. While this procedure maintains a constant composition, it does not allow one to study the effects

of oxygen fugacity and FeO/MgO ratio on phase equilibria.

An alternative is to model an iron-containing system by substituting an analogous component for iron. To be an improvement, the analogue must be insoluble in platinum or silver palladium under experimental conditions and faithfully reproduce the phase relations observed in the natural ferromagnesian system.

Cobalt as an analogue for iron

Cobalt was chosen as an analogue for iron from thermodynamic considerations. Because phase relations and compositions may be predicted from the Gibbs free energy, cobalt is the most likely choice for an analogue to iron (Coons *et al.*, 1976; Navrotsky and Coons, 1976). In addition, CoO–MgO phases generally exhibit nearly ideal solid solution (*e.g.* von Wartenberg and Prophet, 1935; Johnson *et al.*, 1971) as do FeO–MgO phases (*e.g.* Bowen and Schairer, 1935; Nafziger and Muan, 1967). Consequently, ferromagnesian minerals, commonly observed in basaltic systems, should be adequately modelled by analogous cobaltomagnesian phases. Finally, available phase equilibria of cobaltomagnesian–silicate systems are similar to the relations of comparable ferromagnesian silicates, although the equilibria are shifted to higher temperatures (*e.g.* Masse and Muan, 1965; Akimoto *et al.*, 1965). Experiments (Coons *et al.*, 1976) demonstrated that cobalt analogue compositions produce phase relations similar to those observed in the natural ferromagnesian system, even when the composition is as complex as a basalt. Figure 1 summarizes the earlier results, by comparing the one-atmosphere phase relations of the 1921 Kilauea basalt (Hill, 1969) to its cobalt analogue as a function of temperature and $\text{MO}/(\text{M}_2\text{O}_3 + \text{MO})$.² Iron loss was minimized by Hill (1969) by maintaining a large sample/container ratio. In iron-containing systems, the $\text{MO}/(\text{M}_2\text{O}_3 + \text{MO})$ ratio is largely a function of temperature and oxygen fugacity (Hill, 1969). In the analogue system, this ratio is maintained to simulate the effects of oxygen fugacity (see Coons *et al.*, 1976).

With minor exceptions (Coons *et al.*, 1976), the topologies of the phase equilibria of the two systems are very similar. Phase relations of the cobalt analogue are shifted to higher temperature relative to the natural rock relations, reflecting the higher melting

²M refers to either Co or Fe.

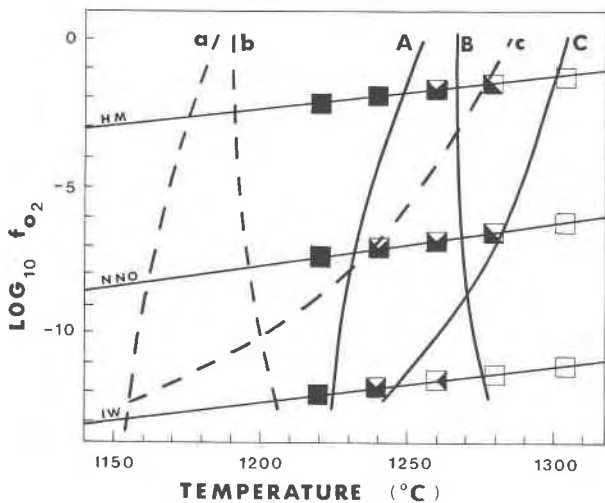


Fig. 1. Comparison of the one-atmosphere phase relations of natural and analogue 1921 Kilauea basalt composition (Coons *et al.*, 1976). Dashed lines = natural composition; solid lines = analogue composition; A and a = disappearance of plagioclase; B = disappearance of olivine; b = disappearance of olivine and clinopyroxene; C = disappearance of clinopyroxene and spinel (liquidus); c = disappearance of spinel (liquidus).

points of cobaltous compounds relative to ferrous compounds.

Platinum wires used to hold the samples were analyzed by electron microprobe after repeated use. The results (Fig. 2) indicated that cobalt loss to platinum is insignificant (less than 7 relative percent) in air at temperatures in excess of 1300°C (Coons *et al.*, 1976). The low value cited above is in good agreement with the theoretical one-atmosphere saturation value of cobalt in platinum (Schwerdtfeger and Muan, 1964). However, it should be noted that the low solubility is a result of the low activity of cobalt metal at the high oxygen fugacity ($10^{-9.7}$) of the experiments. Thus, high-pressure experiments must maintain an elevated oxygen fugacity to maintain the correct $\text{Fe}_2\text{O}_3/\text{CoO}$ ratio and prevent appreciable solubility of cobalt in the container.

While the preliminary experiments demonstrated that cobalt analogue systems produce phase relations topologically similar to those observed in the natural systems, and that cobalt can be prevented from dissolving in the container, no comparison was made of phase complications. A meaningful comparison of corresponding natural and analogue phase compositions can be obtained only at points in space which are precisely defined by the phase assemblage. Accordingly, an analogue to the simple basalt system anorthite–forsterite–magnetite–quartz was investi-

gated for comparison with results obtained by Roeder and Osborn (1966).

Experimental methods

Sample preparation

All starting compositions were synthesized by weighing out appropriate amounts of analytical-reagent-grade oxides and carbonates to yield 10 g batches of desired compositions. Analogue compositions were obtained by equimolar substitution of CoO for FeO. The mixtures were ground for approximately 30 minutes under acetone in an automatic agate ball-mill, then gently dried and fired at 1000°C overnight. Next, the mixtures were subjected to three replicate 3-hour fusions at 1400°C in air and re-ground between each fusion, as above, in acetone. Glasses were analyzed by electron microprobe to check homogeneity. In addition, compositions were checked by X-ray fluorescence analysis, and the glasses were examined for the presence of crystals by standard petrographic techniques. Analyses showed the resulting glasses accurately corresponded with

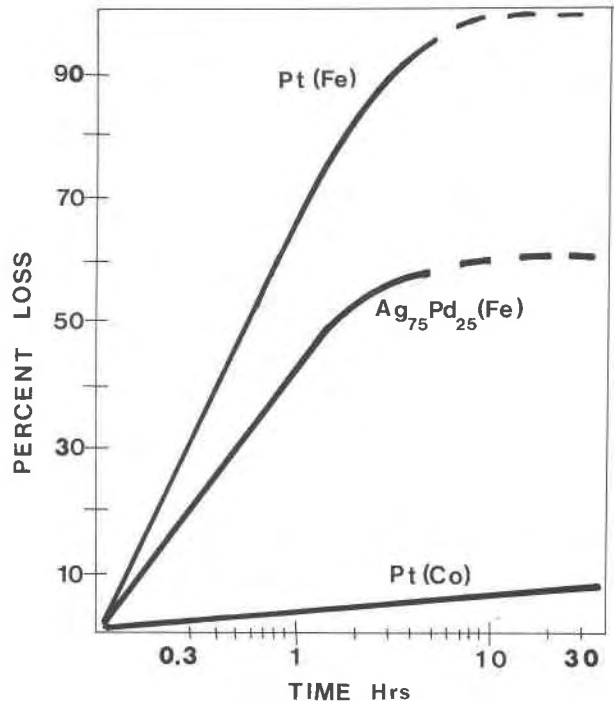


Fig. 2. Relative weight loss of metal to capsule from sample. Pt(Fe) = loss of iron to capsule at 1250°C. $\text{Ag}_{75}\text{Pd}_{25}(\text{Fe})$ = loss of iron to platinum at 1200°C. Pt(Co) = loss of cobalt to platinum at 1350°C. The data for iron loss from platinum are from Merrill and Wyllie (1973) and $\text{Ag}_{75}\text{Pd}_{25}$ from Stern and Wyllie (1975).

the weighed compositions and were homogeneous. Note, however, that microprobe analyses of the glassy products following a single fusion showed gross heterogeneity. Bulk compositions are listed in Table 1.

At one atm CoO and Fe₂O₃ are compatible in air at temperatures in excess of 800°C (see Fig. 3). The overlapping stabilities of CoO and Fe₂O₃ allow the experimenter to simulate any oxygen fugacity of interest. On an isotherm, the effect of varying oxygen fugacity is to alter the relative amounts of polyvalent components (*i.e.* changes the Fe₂O₃/FeO ratio). Thus, analogue compositions may be synthesized with any desired Fe₂O₃/CoO ratio to simulate the effects of oxygen fugacity. Fe₂O₃/FeO molar ratios appropriate for desired temperatures, bulk compositions, and oxygen fugacities were calculated from an equation which was kindly provided by Dr. H. S. Waff and which is presented here with his permission.

$$\log (\text{FeO}_{1.5}/\text{FeO}) = 0.025X(\text{FeO}) + 0.2249 \log f\text{O}_2 + 4550/T^\circ\text{K} - 2.73 \quad (1)$$

(Waff and Weill, in preparation)

where $X(\text{FeO})$ is all iron calculated as the mole fraction of FeO. This relation holds only for compositions which contain less than 8.95 mole percent total alkali. It should be remembered that both cobalt and iron are polyvalent. Therefore care was taken neither to oxidize the CoO nor reduce the Fe₂O₃ components of the mix significantly (see Fig. 3).

Experimental procedure

Small pieces of homogenized glass (~0.07 g) were placed in 0.4 cm diameter loops of 0.05 cm diameter platinum wire and fused into beads with an oxygen-

Table 1. Bulk compositions of starting materials

Oxide	STARTING COMPOSITIONS						
	I	J	K	L	M	O	P
SiO ₂	38.41	42.42	46.28	50.21	54.02	58.04	46.54
Al ₂ O ₃	14.83	14.81	14.81	14.79	14.75	14.76	14.65
Fe ₂ O ₃	1.04	.83	.67	.53	.40	.30	1.28
CoO	23.08	20.79	18.50	16.20	13.87	11.58	23.07
MgO	14.48	13.01	11.59	10.13	8.84	7.21	5.72
CaO	8.16	8.14	8.14	8.14	8.12	8.11	8.06
	S	T	U	W	X	Z	
SiO ₂	46.18	45.81	60.52	55.80	54.96	53.24	
Al ₂ O ₃	14.65	14.65	14.65	14.65	14.65	14.65	
Fe ₂ O ₃	1.01	.70	.05	.13	.34	.37	
CoO	20.88	18.50	2.85	5.70	11.32	11.29	
MgO	8.59	11.45	13.75	15.46	10.31	12.03	
CaO	8.06	8.06	8.06	8.06	8.06	8.06	

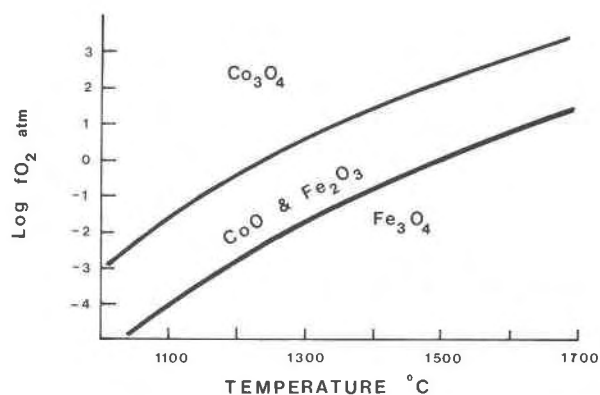


Fig. 3. Stability fields of cobalt and iron oxides as a function of temperature and oxygen fugacity; see text for data sources.

methane torch. Several samples were simultaneously suspended from 0.010 cm platinum quench wire.

Temperature was maintained with a proportional band controller and a silicon-controlled rectifier and monitored with 0.051 cm Pt-Pt₉₀Rh₁₀ thermocouples. The vertical temperature gradient within the hot zone of a vertical silicon-carbide quench furnace was measured and found to be $\pm 1.5^\circ\text{C}$ over 6 cm. Thermocouples used to read temperature were periodically calibrated against a thermocouple certified by the National Bureau of Standards. Constant temperature was maintained and is believed accurate to $\pm 5^\circ\text{C}$. Charges were brought 20°C above liquidus and held for approximately 30 minutes. Temperature was then dropped rapidly to the temperature of interest, where it was held for at least 45 hours. Experiments were terminated by passing an electric current through platinum electrodes and melting the thin quench wire. All charges were quenched into a beaker of water at room temperature.

Each run product was divided into two splits, one for petrographic inspection and one for microprobe analysis. Where possible, the bottom portion of each sample bead was split in half so that stable crystals which had settled during the run could be distinguished from quench crystals which had not settled. Phases were identified using standard optical techniques and verified where necessary by electron microprobe. Portions of platinum wire loops, which had been used repeatedly, were saved and analyzed for cobalt. Owing to the small amount of crystalline material, not all phases observed microscopically were located in the polished slabs prepared for microprobing. When successive grindings and polishings failed to reveal complete phase assemblages, an opti-

cal microscope was used to determine the stable phase assemblage.

Analytical procedure

Microprobe analyses were performed on an automated ARL electron microprobe. Data were generated using a 20 kV accelerating potential and a specimen current in the range of 40 nanoamperes. Machine drift was monitored by analyzing standards of known composition. When analyses were not in the range 100 ± 2 weight percent, the instrument was recalibrated and any data collected over that interval were discarded. Data were reduced using a Bence-Albee (1969) correction. Standards employed were synthetic cobalt diopside glass for CoO, natural orthopyroxene for MgO and SiO₂, synthetic anorthite for CaO and Al₂O₃, and natural ilmenite for FeO. Samples which had previously been analyzed using a Cameca MS 46 electron microprobe and a Co metal standard were reanalyzed using the above procedure. The new analyses were the same, within analytical error, as those reported by Coons *et al.* (1976).³

Equilibrium was tested by duplication of experimental data at the lowest-temperature (1250°C) experiment in runs of different duration. Run durations were in excess of 48 hours for all standard experiments. For the equilibrium test, the experiment lasted 160 hours. All phases were analyzed and compared with those of the 48-hour experiment (see Table 2). Because the results of the two experiments were essentially identical, and because the low-temperature runs will have maximum viscosity (hence the slowest diffusion), runs at higher temperatures made for the same time are also assumed to have

equilibrated. No direct attempt was made to reverse the experiments; therefore the possibility of metastable phases cannot be excluded.

Results and discussion

The phase-equilibria results are listed in Table 3 and shown in Figure 4. For visual presentation, the 6-component system is reduced to a pseudoternary by (1) maintaining the Fe₂O₃/CoO ratio within desired limits; (2) investigating a plane of constant anorthite composition; (3) assuming the Ca/Al ratio in all phases is restricted to the stoichiometric proportions of anorthite (Roeder and Osborn, 1966).

In iron-containing systems the equilibrium ratio of Fe₂O₃ to FeO is largely a function of oxygen fugacity and temperature (see eq. 1). For ease of presentation, Roeder and Osborn (1966) calculated all iron in liquids as Fe₃O₄, thus projecting all compositions onto the magnetite stability surface. In the analogue system, the ferric/ferrous ratio is replaced by Fe₂O₃/CoO, after determining an appropriate composition from equation 1. Allowing for reduction of portions of the Fe₂O₃ component, the effects of oxygen fugacity may be simulated for each bulk composition over a prescribed temperature range without introducing significant error. (For the initial compositions of this study, a temperature range of $\pm 25^\circ\text{C}$ produced an error of less than 0.5 log unit.) Following Roeder and Osborn (1966), analogue liquid compositions were projected to the M₃O₄ oxide surface. This was accomplished by calculating cobalt as a mixed oxide. In other words, cobalt in excess of that needed to account for iron as CoFe₂O₄ was calculated as Co₃O₄.

Comparison of the liquidus diagrams, notably the pseudoinvariant points (Fig. 4), reveals good compositional agreement between the FeO-bearing and analogue systems. The analogue piercing points are located closer to the forsterite apex than are the FeO-

Table 2. Equilibrium test at 1250°C

Oxide	Bulk Composition *	Orthopyroxene				Glass			
		144 Hours		48 Hours		144 Hours		48 Hours	
SiO ₂	60.53	56.95	± .07	57.19	± .12	59.50	± .16	60.14	± .94
Al ₂ O ₃	14.66	1.43	± .15	1.28	± .02	15.95	± .26	15.84	± .12
Fe ₂ O ₃	.06	.05	± .04			.14	± .02	.13	± .04
CoO	2.86	4.79	± .02	4.68	± .08	2.80	± .02	2.85	± .11
MgO	13.75	36.02	± .24	35.97	± .06	10.62	± .01	10.22	± .19
CaO	8.06	.27	± .01	.26	± .00	9.13	± .03	9.09	± .04

* Associated weighing error less than .01 wt %

± Indicates standard error of four analyses

Table 3. Summary of results of phase equilibria experiments on simple basalt composition

Run	Temperature (°C)	Experiment Duration (Hrs.)	Sample	Phases Present	Comments
8	1340	51	I-2	oliv, ox, glass	0 - 5% crystal
			J-2	oliv, ox, glass	0 - 5% crystal
			K-2	glass	
			L-1	glass	
			M-1	glass	
8	1330	72	O-1	glass	
			I-3	oliv, ox, glass	plag?
9	1310	48	J-3	oliv, ox, glass	plag?
			K-3	opx, glass	oliv? - 20% crystal
10	1350	50	L-2	glass	qtz?
			M-2	glass	qtz?
14	1265	56	I-4	oliv, glass, plag	
			J-4	oliv, glass	
15	1275	52	J-4	oliv, ox, glass	opx? - 30% crystal
			K-5	oliv, opx, ox, glass	50% crystal
16	1285	49	L-4	opx?, glass	
			M-3	glass	
18	1250	74	L-5	opx, glass	cpx?
			L-6	opx, glass	0 - 5% crystal
19	1290	90	P-1	opx, glass	
			S-1	ox, opx, glass	
			T-1	ox, glass	opx?
			P-2	glass	
			S-2	ox, glass	10 - 20% crystal
20	1290	83	T-2	ox, glass	opx?
			P-3	ox?, plag	12% crystal
21	1310	48	S-3	ox, glass	18% crystal
			S-4	ox, glass	12% crystal
23	1325	50	T-3	opx, glass	7% crystal
			T-5	oliv, ox, glass	3% crystal
24	1295	68	U-2	plag, glass	less than 1% crystal
			W-2	opx, glass	trid?
			O-2	glass	
26	1315	95	U-3	glass	opx?, plag?
			W-3	opx, glass	6% crystal
			X-3	opx, glass	8% crystal
27	1299	66	J-9	oliv, ox?, glass	
28	1220	74	O-3	trid, glass	3% crystal

bearing piercing points. This is a consequence of the greater partitioning of CoO into olivine and pyroxene as compared to FeO. For instance, K_D CoO/MgO for olivine/liquid⁴ is 0.61 (Coons *et al.*, 1976), while K_D FeO/MgO olivine/liquid is 0.30 (Roeder and Emslie, 1970).

An improved approximation to FeO-bearing liquid compositions may be made by correction through these distribution constants, provided either olivine or orthopyroxene is an equilibrium phase. The proce-

cedure assumes that deviation from FeO-bearing compositions arises solely from the unequal partitioning of MO (where M = Fe or Co), as cited above. This is justified, in part, by recognizing that the analogue liquid compositions precisely reflect those of the FeO-bearing system except for the MO/MgO ratio.

Correction of the analogue liquid composition

In the correction procedure, the first step is to convert the experimentally-derived analogue composition to molar quantities. The total number of moles is considered fixed, and only the molar ratio of CoO/MgO is variable. In this case it was necessary to esti-

⁴ K_D MO/MgO for ol/liq refers to the molar exchange reaction: MO (ol) + MgO (liq) = MgO (ol) + MO (liq).

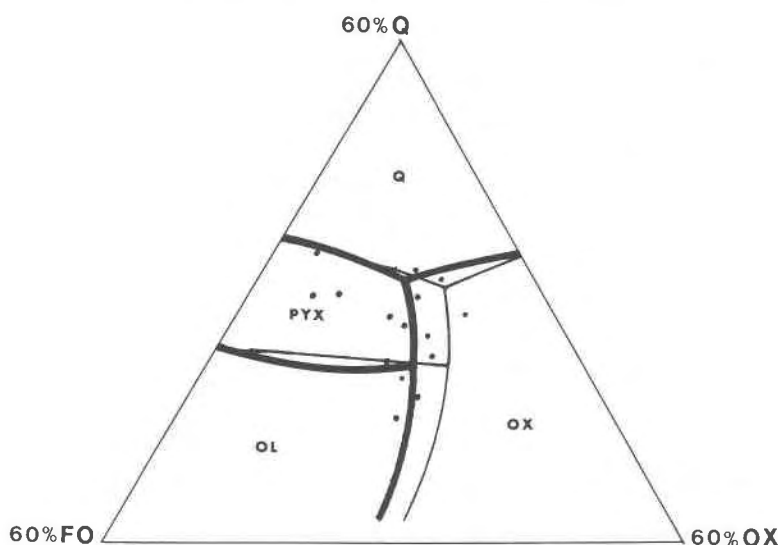


Fig. 4. Comparison of analogue and natural liquidus relations for the simple basalt on the $An = 40$ wt % plane at $\log f_{O_2} = -9.0$. Light lines = natural system (Roeder and Osborn, 1966); heavy lines = analogue system; dots = data points, this study.

mate the olivine composition at the olivine–pyroxene–magnetite piercing point in the iron-bearing system (Roeder and Osborn, 1966). This was accomplished by first calculating the Fe_2O_3/FeO ratio of the liquid at an oxygen fugacity of 10^{-9} bars from equation 1 (Waff and Weill, in preparation). Then the equilibrium olivine composition was estimated from K_D FeO/MgO olivine/liquid = 0.30 (Roeder and Emslie, 1970). The resulting olivine composition is 69.2 mole percent forsterite. Redistribution of CoO and MgO in the analogue liquid to conform to the ferromagnesian equilibrium ratio results in the corrected analogue composition shown in Table 4. For reference, the estimated composition for the FeO -bearing system (Roeder and Osborn, 1966) is also shown, along with the absolute difference. The agreement is exceptionally good and reflects the well-characterized nature of olivine–liquid cation distribution. A similar correction for the analogue pseudo-invariant liquid composition in equilibrium with orthopyroxene–quartz–magnetite is also shown in Table 4. The agreement with the estimated FeO -bearing composition is not as good as that for the assemblage containing olivine. This is attributed to the less well-known nature of orthopyroxene–liquid cation distribution.

The best use of the cobalt analogue technique, as above, occurs when the natural olivine or orthopyroxene composition is known or can be independently estimated. However, the analogue system may be used as an effective model for natural liquid compositions as long as olivine or orthopyroxene are

stable—even if there is no prior estimate of their equilibrium compositions. In these cases a bracketing model is utilized. The minimum FeO/MgO ratio occurs as the direct analogue of the experimental composition (*i.e.* $CoO = FeO$). The maximum FeO/MgO ratio arises from applying the equilibrium ratio for the ferromagnesian distribution (*e.g.* 0.30 for olivine/liquid) to the composition of the experimentally-determined analogue phase. The natural liquid composition must lie between these two extremes. Figure 5 demonstrates the effectiveness of this approach.

It is notable that this correction procedure will hold at all pressures up to 35 kbar, and perhaps higher. Experiments conducted at pressures to 35 kbar show no change in K_D CoO/MgO for either olivine or orthopyroxene (Coons, 1978). By inference,

Table 4. Analogue liquid compositions after correction

Oxide	Corrected analogue liquid	Iron-bearing liquid	Absolute deviation
Correction using olivine; $K_D = 0.30$			
SiO_2	44.97	44.34	+0.63
Al_2O_3	13.99	14.66	-0.67
Fe_2O_3	5.34	4.52	+0.82
1FeO	20.38	19.82	+0.56
MgO	7.40	7.80	-0.40
CaO	7.78	8.06	-0.28
Correction using orthopyroxene; $K_D = 0.23$			
SiO_2	53.79	53.18	+0.61
Al_2O_3	14.49	14.66	-0.17
Fe_2O_3	1.87	2.69	-0.82
1FeO	17.07	15.89	+1.18
MgO	4.82	5.50	-0.68
CaO	7.97	8.06	-0.09

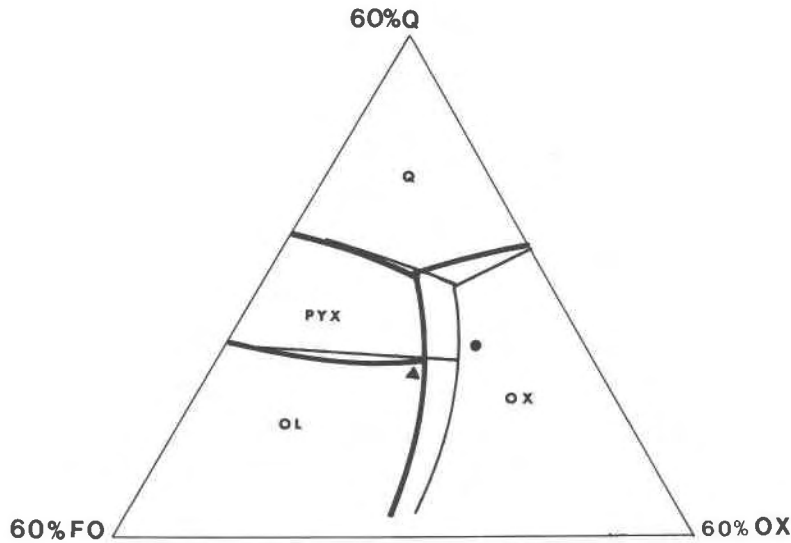


Fig. 5. Model correction of the invariant analogue liquid composition using an experimental olivine. Light lines = natural system (Roeder and Osborn, 1966); heavy lines = analogue system; ▲ = experimental liquid composition containing analogue olivine (minimum model composition); ● = maximum model composition.

this confirms Roeder and Emslie's (1970) suspicions that K_D FeO/MgO would not be pressure-dependent. It is contrary to Mysen's (1975) findings that K_D FeO/MgO varies as a function of $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio and pressure. While Mysen's experiments were water-saturated, it seems more likely that the source of disagreement lies in the uncertainty of his $\text{Fe}_2\text{O}_3/\text{FeO}$ (hence, FeO/MgO) determination. It should be emphasized that any change in K_D must be caused by a phenomenon which affects FeO (or CoO) and MgO to different extents.

One of the recurrent differences between cobaltomagnesian and ferromagnesian phase relations is the higher melting temperatures in the analogue system. It may be possible to approximate the equilibrium temperature of natural relations from analogue results because of the thermal dependence of MO distribution between silicate and liquid. Linear regression analysis for MO distribution between olivine and liquid is available for FeO (Roeder and Emslie, 1970) and has been performed on available data for CoO (Leeman, 1974; Coons *et al.*, 1976; Coons, 1978). The resulting motor distributions ($D_{\text{MO}} = \text{MO olivine}/\text{MO liquid}$) give rise to the following expressions for converting temperatures from analogue to natural and natural to analogue systems respectively.

$$\log D^* \text{CoO} = 4.04x - 2.45 \quad (2)$$

$$\log D^* \text{FeO} = 3.91x - 2.51 \quad (3)$$

where $x = 1000/T^\circ\text{K}$ and $D^* = \text{corrected DMO}$.

Approximating the equilibrium temperatures of a ferromagnesian system from an analogue experiment requires three steps:

- (1) Analyze the coexisting phases to determine the molar ratio.
- (2) Multiply this ratio by two to account for the difference in MO partitioning (*i.e.* taking MgO as a reference K_D , $\text{CoO} = 0.61$, K_D FeO = 0.30, and $0.61/0.30 \approx 2.0$). This value is D^* .
- (3) Substitute into equation 2 for D^* and solve for temperature.

For example, analysis of coexisting olivine and liquid located near invariant point X yields $D_{\text{CoO}} = 25.15/14.86 = 1.6925$. Multiplication by two and substitution into equation 2 yields a temperature of 1203°C (as opposed to the actual temperature for the analogue experiment of 1299°C). This compares with an estimate of $1190 \pm 5^\circ\text{C}$ for the corresponding FeO-bearing invariant point (Roeder and Osborn, 1971).

It should be emphasized that the equations listed above for temperature estimation apply only to one-atm experiments. It has been clearly demonstrated that the linear temperature-dependence of simple distribution ratios for olivine/liquid pairs varies with pressure and changing bulk composition (Leeman, 1978).

Conclusion

We have demonstrated that at one atm CoO-containing systems are useful analogues of FeO-bearing systems. The chemography of the melting relations

for the two systems is nearly identical, and liquid compositions are correctable. Analogue compositions may be maintained constant by conducting experiments at an elevated oxygen fugacity, which also allows simulation of different $\text{Fe}_2\text{O}_3/\text{FeO}$ ratios.

Available high-pressure data indicate that approximation of ferromagnesian compositions by cobalt-magnesian compositions remains valid. Phase transitions of geologically important phases appear to be very similar (Akimoto *et al.*, 1965, 1969; Ringwood, 1968; Navrotsky and Kasper, 1976), and use of the analogue at high pressure has met with success (Eggler and Wendlandt, 1977). We therefore conclude that the cobalt analogue technique provides a flexible alternative for modeling ferromagnesian systems when iron loss would otherwise prevent accurate determinations. Some conditions and procedures which will aid in producing and interpreting successful cobalt analogue experiments follow.

(1) Reactions occur on a molar (not weight) basis. Therefore, to simulate an iron-containing composition, CoO should be substituted for FeO in equimolar amounts.

(2) Both Co and Fe form polyvalent oxides. Care must be taken to stay within the prescribed range of $f\text{O}_2$ and composition (see Fig. 3 and eq. 1).

(3) Some crystalline phases (*e.g.* olivine, orthopyroxene) will reduce Fe_2O_3 to FeO and incorporate the 2+ state in their structure. When using distribution coefficients *etc.* to correct compositions, FeO + CoO should be considered a single component.

(4) Because of the fractionation of CoO and Fe_2O_3 , their ratio in the liquid will change with the ratio of crystal/liquid. If the purpose of the experiment is to simulate a fixed oxygen fugacity, crystallization should be minimized.

(5) Cobalt analogue compositions quench to brightly colored phases, shades of either red or blue, depending on the coordination of the cobalt ion. This facilitates phase identification. However, the depth of the coloration will depend on the amount of cobalt in the phase as well as the thickness of the grain. Therefore, optimum phase contrast will appear in thin section, where crystal thicknesses will be approximately equal.

(6) Identification of unstable quench crystals is often quite simple in analogue systems. In our experience, quench phases tend to be clustered together and appear as very small crystals connected by blue glass. When the quench phases are of larger size they often contain streaks of blue, suggesting the presence of glassy material.

(7) When selecting compositions for investigation of ferromagnesian systems, it should be remembered that CoO will be partitioned into crystalline phases (at approximately twice the amount of FeO). This causes shifts away from the 'FeO' end of phase diagrams.

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References

- Akimoto, S., T. Katsura, Y. Syono, H. Fujisawa and E. Komada (1965) Polymorphic transition of pyroxenes FeSiO_3 and CoSiO_3 at high pressures and temperatures. *J. Geophys. Res.*, 70, 5269-5278.
- , Y. Matsui and Y. Sato (1969) High pressure transformation in Co_2SiO_4 olivine and some geophysical implications. *Phys. Earth Planet. Interiors*, 1, 498-504.
- Bence, A. E. and A. L. Albee (1969) Empirical correction factors for the electron microanalysis of silicates and oxides. *J. Geol.*, 76, 382-403.
- Biggar, G. M. (1970) Molybdenum as a container for melts containing iron oxide. *Ceram. Bull.*, 49, 286-289.
- Bowen, N. L. and J. F. Schairer (1935) The system $\text{MgO}-\text{FeO}-\text{SiO}_2$. *Am. J. Sci.*, 29, 151-217.
- Coons, W. E. (1978) *Cobalt as an Analogue for Iron during High Temperature Experiments on Basaltic Compositions*. Ph.D. Thesis, Arizona State University, Tempe, Arizona.
- , J. R. Holloway and A. Navrotsky (1976) Co^{2+} as a chemical analogue for Fe^{2+} in high temperature experiments in basaltic systems. *Earth Planet. Sci. Lett.*, 30, 303-308.
- Eggler, D. H. and R. F. Wendlandt (1977) Experimental studies on the relationship between kimberlite magmas and partial melting of peridotite (abstr.). *Second Int. Kimberlite Conf., Santa Fe, New Mexico, Extended Abstracts*.
- Helz, R. T. (1973) Phase relations in basalts in their melting range at $P(\text{H}_2\text{O}) = 5$ kbar as a function of oxygen fugacity. *J. Petrol.*, 14, 249-302.
- Hill, R. E. T. (1969) *The Crystallization of Basaltic Melts as a Function of Oxygen Fugacity*. Ph.D. Thesis, Queen's University, Kingston, Ontario, Canada.
- Holloway, J. R. and C. W. Burnham (1972) Melting relations of basalt with equilibrium water pressure less than total pressure. *J. Petrol.*, 13, 1-29.
- Johnson, R. E., E. Woermann and A. Muan (1971) Equilibrium in the system $\text{MgO}-\text{FeO}-\text{TiO}_2$. *Am. J. Sci.*, 271, 278-287.
- Kesson, S. E. (1974) Petrogenesis of high-Ti mare basalts: melting of 70215 in vacuum and at high pressures. *EOS*, 56, 1200.
- Leeman, W. P. (1974) *Experimental Determination of Partitioning of Divalent Cations between Olivine and Basaltic Liquid*. Ph.D. Thesis, University of Oregon, Eugene, Oregon.
- (1978) Distribution of Mg^{2+} between olivine and silicate

- melt, and its implications regarding melt structure. *Geochim. Cosmochim. Acta*, 42, 789–800.
- Masse, D. P. and A. Muan (1965) Phase equilibria at liquidus temperatures in the system cobalt oxide–iron oxide–silica in air. *J. Am. Ceram. Soc.*, 48, 466–469.
- Merrill, R. B. and P. J. Wyllie (1973) Absorption of iron by platinum capsules in high-pressure rock melting experiments. *Am. Mineral.*, 58, 16–23.
- Mysen, B. O. (1975) Partitioning of iron and magnesium between crystals and partial melts in peridotite upper mantle. *Contrib. Mineral. Petrol.*, 52, 69–74.
- Navrotsky, A. and W. E. Coons (1976) Thermochemistry of some pyroxenes and related compounds. *Geochim. Cosmochim. Acta*, 40, 1281–1288.
- and R. Kasper (1976) Spinel disproportionation at high pressure: calorimetric determination of enthalpy of formation of Mg_2SnO_4 and Co_2SnO_4 and some implications for silicates. *Earth Planet. Sci. Lett.*, 31, 247–254.
- Ringwood, A. E. (1963) Olivine spinel transformation in Co orthosilicate. *Nature*, 198, 79–80.
- (1968) Phase transformations in the mantle. *Earth Planet. Sci. Lett.*, 5, 401–412.
- Roeder, P. L. and R. F. Emslie (1970) Olivine–liquid equilibrium. *Contrib. Mineral. Petrol.*, 29, 275–281.
- and E. F. Osborn (1966) Experimental data for the system $MgO-FeO-Fe_2O_3-CaAl_2Si_2O_8$ and their petrologic implications. *Am. J. Sci.*, 264, 428–440.
- Schwerdtfeger, K. and A. Muan (1964) Thermodynamics of platinum–cobalt alloys. *Acta Metallurgica*, 12, 905–911.
- Stern, C. R. and P. J. Wyllie (1975) Effect of iron absorption in rock melting experiments at 30 kbar. *Am. Mineral.*, 60, 681–690.
- von Wartenberg, H. and E. Prophet (1932) Melting point diagrams of highly refractory oxides. *Z. anorg. allgem. Chem.*, 208, 369–379.
- Walker, D., J. Longhi and J. F. Hays (1972) Experimental petrology and origin of Fra Mauro rocks and soil. *Proc. Third Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl.* 3, 797–813.

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