Phase Relations in the CaO-IrO₂-Ir System in Air

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The equilibrium phase relations for the CaO-IrO₂-Ir system were determined in air using the quenching technique. The system contains three stable compounds $4CaO \cdot IrO_2$, $2CaO \cdot IrO_2$, and $CaO \cdot IrO_2$; they dissociate to an oxide phase, Ir metal, and oxygen at 1240, 1170, and 1135°C, respectively. A metastable form of CaO · IrO₂ occurs at temperatures between 900 and 1100°C. Indexed X-ray diffraction powder patterns of all compounds are given.

1. Introduction

This study was initiated as part of a general program of phase equilibrium investigations involving the alkaline earth and other oxides with the Pt-group metal oxides (1-3). These systems have practical importance since Pt-group metals are used extensively for container materials and other high temperature applications. Presented here are equilibrium relationships of the condensed phases in the system CaO-IrO₂-Ir in air.

2. Experimental Procedure

Specimens were prepared from 0.4 g batches of various combinations of calcium carbonate and IrO_2 , each having a purity of at least 99.6%. Calculated amounts of each end member, corrected for ignition loss, were weighed to the nearest milligram. Each batch was thoroughly hand mixed and calcined in a muffle furnace at a minimum temperature of 800°C, or heated directly at the temperature of interest. Specimen containers were open gold tubes and open or welded platinum tubes; no apparent reaction occurred with the various oxide samples. Portions of each calcined batch were refired in a platinum alloy wire-wound quench furnace at various temperatures for different periods of time, and quenched in ice water or air. Temperatures in the quench furnace were measured with a Pt-Pt, 10% Rh calibrated thermocouple. All furnace temperatures¹ are considered accurate to $\pm 5^{\circ}$ C. The

Key Words: CaO: IrO_2 compounds, CaO- IrO_2 -Ir system, dissociation, equilibrium, phase relations.

¹ This scale (IPTS 1968) applies to all temperatures listed in this paper.

precision of the measurements was estimated to be $\pm 2^{\circ}C$.

Equilibrium was assumed when the X-ray pattern showed no change after successive heat treatments. The stability of a compound was established by heating first above and then below the dissociation temperature. Stable compounds always reformed from the dissociation products; if prolonged heating failed to reform the phase, it was assumed to be metastable, forming only on heating. All specimens were examined by X-ray diffraction at room temperature with a high-angle-recording Geiger counter diffractometer and Ni-filtered Cu radiation. The scanning rate was $1/4^{\circ} 2\theta/\min$. Unit cell dimensions were refined by a least-squares computer program² and estimated accurate to at least 2 in the last decimal place.

3. Results and Discussion

The equilibrium phase diagram in air, Fig. 1, was constructed from the data in Table I. Oxygen reaction lines are dashed, and A through E indicate tie lines. The three phase triangular areas with listed temperatures represent invariant situations where three condensed phases coexist in equilibrium with oxygen. The oxygen reaction lines connect compositions on the CaO-IrO₂ join and the final compositions attained on dissociation of the oxide mixtures. It should be emphasized that the dissociation products are condensed phases always in equilibrium with oxygen.

² H. T. Evans Jr., D. E. Appleman, and D. S. Handwerker, Amer. Crystal. Assoc. Annual Meeting, Cambridge, MA Program, 43–43.



FIG. 1. Phase equilibrium diagram for the CaO-IrO₂-Ir System in Air. Compositions and temperatures of experiments. Oxygen reaction lines are dashed. A through E indicate tie lines for given temperatures: $A = 1021^{\circ}$ C; 1021° C $< B < 1135^{\circ}$ C; 1135° C $< C < 1170^{\circ}$ C; 1170° C $< D < 1240^{\circ}$ C; $E = >1240^{\circ}$ C.

The binary-type phase diagram in the top portion of Fig. 1 is a projection of certain elements of the three dimensional ternary system CaO-IrO₂-Ir on a two dimensional plane figure; it represents a composite of the CaO-Ir and CaO-IrO₂ systems. As the temperature is increased, the compositions of the solid phases change by an apparent oxygen loss to those indicated by the CaO-Ir join. Illustrating a dissociation as a type of phase transition or decomposition in which vapor phase is ignored gives a simple binary representation of the ternary phase relations. This method of representation has been used by other investigators and is discussed in detail (1, 4).

THE CaO– IrO_2 –Ir system

TABLE I

EXPERIMENTAL DATA FOR COMPOSITIONS IN THE CaO-IrO2-Ir System

Composition		Heat Treatment				
4 0	Ir02	Previous ^e Final		X-ray diffraction analyses ^b	Remarks	
101%	No17	°C-hr	*C-hr			
90	10		1000-72	2Ca0-1r02+Ca0		
		1000-72	1000-20	2Cm0+1r02+Cm0		
		1000-72,1000-20	1100-96	Ca0+4Ca0 · Ir02+2Ca0 · 1r02	nonequilibrium	
		1000-72,1000-20	1200-18 ⁰	Ca0+4Ca0-1r02		
		1000-72,1000-20	1300-2	Ca0,Ir		
80	20		1000-72	2Ca0-1+02+Ca0		
		1000-72	1000-20	2Ca0-1r02+Ca0		
		1000-72,1000-20,1200-20	1000-144	4Ce0.1r02		
		1000-72,1000-20	1100-96	2Ca0-1r02+Ca0+4Ca0-1r02	nonequilibrium	
		1000-72,1000-20	1200-1	4CaO·1rO ₂ +unidentified phase	Quenched in ice water; unidentified phase probably a hyd	
		1000-72,1000-20	1200-18 ^c	4Ca0+1r02+Ca0		
		1000-72,1000-20,1300-2	1200-20	4Ca0-1r02	4CaO IrO2 formed from CaO+Ir	
		1000-72,1000-20	1225-2	4Ca0.1r02		
		1000-72,1000-20	1230-2	4Ca0.1r02		
		1000-72,1000-20	1235-2	4Ca0 1r02		
		1000-72,1000-20	1240-2	4Ca0'1r02+Ca0+Ir		
		1000-72,1000-20	1250-2	Ca0+4Ca0 · Ir02+Ir	nonequilibrium	
		1000-72,1000-20	1300-2	CaO+1r		
75	25		1000-20	2Ca0-1r0 ₂ +Ca0		
		1000-20	1000-22	2CaO 1r02+Ca0		
		1000-20,1000-22	1080-18	2Ca0-1r02+Ca0		
		1000-20,1000-22	1200-3	4Ca0-Ir02+2Ca0-Ir02+Ca0	nonequilibrium	
66.6	33.3		1000-18	2C#0·IT02+C#0		
		1000-18	1000-18	2CeO-IrO2		
		1000-18,1000-18,1300-2	1000-95	2CaO·IrO2	2CaO·1rO2 formed from CaO+1r	
		1000-18,1000-18	1075-20	2CaO·Ir0 ₂		
		1000-18,1000-18	1075-120 ^C	2Ca0-1r02		
		1000-18,1000-18	1075-360 ^C	2Ca0·1r02		
		1000-18,1000-18	1165-18	2CeO·IrO2		
		1000-18,1000-18	1170-19	2CaO · 1r02+4CaO · 1r02		
		1000-18,1000-18	1190-18	2CaO·IrO2+4CaO·IrO2+Ir+CaO	nonequilibrium	
		1000-18,1000-18	1210-2	2CaO·IrO2+4CaO·IrO2+CaO	nonequilibrium	
		1000-18,1000-18	1220-2	2CmO·IrO2+4CmO·IrO2+CmO	nonequilibrium	
		1000-18,1000-18	1220-96	4Ca0.1r02+2Ca0.1r02+1r	nonequilibrium	
		1000-18,1000-18	1225-2	2Ce0.1r02+4Ca0.1r02+Ca0	nonequilibrium	
		1000-18,1000-18	1230-2	2Ca0.1r02+4Ca0.1r02+1r+Ca0	nonequilibrium	
		1000-18,1000-18	1240-2	4Ca0.1r02+Ca0+1r		
		1000-18,1000-18	1260-2	CaO+Ir+4CaO·Ir02	nonequilibrium	
		1000-18,1000-18	1300-2	CaO+1r		
60	40		900-18	2CmO-1r02+1r02		
		900-18	1050-192	2CmO-ir0 ₂ +ir		
50	50		800-18	2CaO·IrO2+IrO2		
		1000-18,1000-19,1300-2	800-96	Ca0.Ir02+2Ca0.Ir02+1r02	nonequilibrium	
		800-18	850-18	2Ca0-Ir0,+1r0,		
			900-1	2Ca0 . Ir0,+H-Ca0 . Ir0,+Ca0 . Ir0,	nonequilibrium	
		800-18,850-18	900-20	2CaO·IrO2+H-CaO·IrO2+IrO2+CaO·IrO2	nonequilibrium	
		1000-18,1000-19,1300-2	900-24	Ca0.Ir02+2Ca0.Ir02	CaO·IrO ₂ formed from CaO+Ir; trac. amount of 2CaO·IrO ₂	
			950-2	M-CaO·IrO2+CaO·IrO2	nonequilibrium	
		800-18,850-18,900-20	950-120	CaO·IrO2+M-CaO·IrO2	nonequilibrium	
			1000-1	M-CaO·lrO2+CaO·lrO2	nonequilibrium	
			1000-2	M-CaO IrO2+CaO IrO2	nonequilibrium	
			1000-3	CaO·IrO2+M-CaO·IrO2	nonequilibrium	
		1000-20 ^d ,1000-22 ^d	1000-18 ^d	M-CaO·IrO2+CaO·IrO2+2CaO·IrO2	nonequilibrium	
			1000-18	M-Ca0.Ir02+2Ca0.Ir02+Ir05	nonequilibrium	
		1000-18,1000-19,1300-2	1000-19	Ca0.1r02+2Ca0.1r02	M-CaO·IrO ₂ failed to form from GaO+Ir	
			1000-19	CaO-1r0,+M-CaO-1+0_	nonequilibrium	
			1000-19	Ca0.110-+H-Ca0.1+6-	alow cooled: nonenuitibetum	
		1000 10	1000.10	2		
		1000-18	1000-19	N-CaO·(rO ₂ +2CeO·TrO_+CaO·TrO	nonequilibrium	

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TABLE I—continued

0 17.02 Product ⁶ Findl X-ray differentian analyses ⁵ Remarks 11 Moll X-ray Scher Sc	nc		Reat Treatment"					
11 10.1 °C·hr °C·hr 0 50 1000-20 ⁴ 1000-21 ⁴ McDo'16y/2Ca0':10y/2Ca0':10y menegalibrian 90-12,550-13,550-13,500-20, 99-120 1075-15 ⁴ Ca0':10y/2Ca0':10y/McCa0':10y menegalibrian 91-120 1075-15 ⁴ Ca0':10y/4Ca0':10y/McCa0':10y menegalibrian menegalibrian 950-120 1075-15 ⁴ Ca0':10y/4Ca0':10y/McCa0':10y menegalibrian menegalibrian 1000-13,1000-19 1075-10 Ca0':10y/4Ca0':10y/2Ca0':10y menegalibrian menegalibrian 1000-13,1000-19 1075-10 Ca0':10y/4Ca0':10y/2Ca0':10y menegalibrian menegalibrian 1000-13,1000-19 1100-1 McCa0':10y/4Ca0':10y menegalibrian menegalibrian 1000-13,1000-19 1100-1 McCa0':10y/4Ca0':10y menegalibrian menegalibrian 1000-13,1000-19 1100-1 McCa0':10y/4Ca0':10y menegalibrian 1000-13,1000-19 1100-2 Ca0':10y/4Ca0':10y menegalibrian 1000-13,1000-19 1100-2 Ca0':10y/4Ca0':10y menegalibrian 1000-10,1000-19<	J ₂		Previous ^e Final		X-ray diffraction analyses ^b	Remarks		
0 50 1000-25 ^d 1000-25 ^d R-Ga0-Irtog+Ga0-Irog+Ca0-Irog posequilibrium 900-13, 950-13, 950-20, 950-120 1075-13 Ga0-Irog+Ca0-Irog+Ca0-Irog monequilibrium 900-13, 1000-19, 1000-19 1075-13 ^d Ga0-Irog+Ca0-Irog+Ca0-Irog monequilibrium 1000-18, 1000-19 1075-13 ^d Ga0-Irog+Ca0-Irog+Ca0-Irog monequilibrium 1000-18, 1000-19 1075-13 ^d Ga0-Irog+Ca0-Irog Trace ansum of Za0-Iri 1000-18, 1000-19 1075-13 ^d Ga0-Irog+Ca0-Irog+Ca0-Irog Romequilibrium 1000-18, 1000-19 1075-13 ^d Ga0-Irog+Ca0-Irog+Ca0-Irog Romequilibrium 1000-18, 1000-19 1075-13 ^d Ga0-Irog+Ca0-Irog+Ca0-Irog Romequilibrium 900-10, 950-120 1100-13 Ca0-Irog+Ca0-Irog Romequilibrium 900-20, 950-120 1130-2 Ca0-Irog+Ca0-Irog Romequilibrium 900-10, 950-120 1130-2 Ca0-Irog+Ca0-Irog Romequilibrium 900-20, 950-120 1135-2 Ca0-Irog+Ca0-Irog Romequilibrium 900-20, 950-120 1135-2 Ca0-Irog+Ca0-Irog+Tr Romequilibrium	17.		°C-hr	°C-hr				
00-16,800-18,900-20, 990-120 1075-18 Ca0-160_2-2Ca0-170_2+M-Ca0-170_2 1000-18,900-19,100-19 1075-120 Ca0-170_2+Ca0-170_2+Ca0-170_2 1000-18,1000-19 nonequilibrium 1000-18,1000-19 1075-120 Ca0-170_2+Ca0-170_2+Ca0-170_2 1000-18,1000-19 nonequilibrium 1000-18,1000-19 1075-120 Ca0-170_2+Ca0-170_2+Ca0-170_2 1000-18,1000-19 N-Ca0-170_2+Ca0-170_2+Ca0-170_2 1000-18,1000-19 N-Ca0-170_2+Ca0-170_2+Ca0-170_2 1000-18,1000-19 N-Ca0-170_2+Ca0-170_2+Ca0-170_2 1000-18,1000-19 N-Ca0-170_2+Ca0-170_2+Ca0-170_2 1000-18,100-19 N-Ca0-170_2+Ca0-170_2+Ca0-170_2 1000-18,100-19 N-Ca0-170_2+Ca0-170_2+Ca0-170_2 1000-18,100-19 N-Ca0-170_2+Ca0-170_2+Ca0-170_2 Trace amount of 2Ca0-170 2Ca0-170_2+Ca0-170_2+Ca0-170_2 Trace amount of 2Ca0-170 2Ca0-170_2+Ca0-170_2+Ca0-170_2+Ca0-170_2 Trace amount of 2Ca0-170 2Ca0-170_2+Ca0-170_2+Ca0-170_2+Ca0-170_2 Trace amount of 2Ca0-170 2Ca0-170_2+Ca0)	1000	20 ^d	1000-22 ^d	M-Ca0.1r02+Ca0.1r02+2Ca0.1r05	ponequilibrium		
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800-18,830-18, 1100-18 C40'IFQ_+MC40'IFQ_+Z40'IFQ_ nonequilibrias 800-18,850-18, 1100-19 2Ca0'IFQ_+MC40'IFQ_ nonequilibrias 800-18,850-18, 900-20,950-120 1120-2 Ca0'IFQ_+MC40'IFQ_ trace amount of 2Ca0'IFQ 800-18,850-18, 900-20,950-120 1130-2 Ca0'IFQ_+ZCa0'IFQ_ trace amount of 2Ca0'IFQ 800-18,850-18, 900-20,950-120 1135-2 Ca0'IFQ_+ZCa0'IFQ_ trace amount of 2Ca0'IFQ 800-18,850-18, 900-20,950-120 1155-2 Ca0'IFQ_+ZCa0'IFQ_IFF nonequilibrias 800-18,850-18, 900-20,950-120 1150-2 Ca0'IFQ_+ZCa0'IFQ_IFF nonequilibrias 800-18,850-18, 900-20,950-120 1150-2 ZCa0'IFQ_+TCA0'I		1000	18,1000-19	1100-3	N-Ca0'IrO2+Ca0'IrO2+2Ca0'IrO2	nonequilibrium		
900-20,950-120 1100-18 Ca0 TrO2+TK-Ca0 TrO2 nonequilibrius 1300-2 1100-18 Ca0 TrO2+TK-Ca0 TrO2 nonequilibrius 800-18,850-18, 900-20,950-120 1120-2 Ca0 TrO2+ZCa0 TrO2 trace amount of ZCa0 TrO 900-20,950-120 1130-2 Ca0 TrO2+ZCa0 TrO2 trace amount of ZCa0 TrO 900-20,950-120 1130-2 Ca0 TrO2+ZCa0 TrO2 trace amount of ZCa0 TrO 900-20,950-120 1135-2 Ca0 TrO2+ZCa0 TrO2 trace amount of ZCa0 TrO 900-20,950-120 1135-2 Ca0 TrO2+ZCa0 TrO2 trace amount of ZCa0 TrO 900-20,950-120 1150-2 Ca0 TrO2+ZCa0 TrO2 nonequilibrius 800-18,850-18, 900-20,950-120 1150-2 Ca0 TrO2+TC nonequilibrius 900-20,950-120 1175-2 ZCa0 TrO2+Tr nonequilibrius 900-20,950-120 1175-2 ZCa0 TrO2+Tr nonequilibrius 900-20,950-120 1070-2 ZCa0 TrO2+Tr nonequilibrius 900-18,1000-19 1300-2 TrCa0 nonequilibrius 900-18,1000-19 1300-2 TrCa0 TrO2+Ca0 TrO2 <		800-	8,850-18,					
1300-2 1100-19 2Ca0·1r0y+1r4Ca0·1r0y nomequilibrium 800-18,650-18, 900-20,950-120 1120-2 Ca0·1r0y+2Ca0·1r0y trace amount of 2Ca0·1r0 900-20,950-120 1130-2 Ca0·1r0y+2Ca0·1r0y trace amount of 2Ca0·1r0 900-20,950-120 1130-2 Ca0·1r0y+2Ca0·1r0y trace amount of 2Ca0·1r0 900-20,950-120 1130-2 Ca0·1r0y+2Ca0·1r0y nomequilibrium 900-20,950-120 1150-2 Ca0·1r0y+2Ca0·1r0y nomequilibrium 900-20,950-120 1150-2 Ca0·1r0y+2Ca0·1r0y nomequilibrium 900-20,950-120 1150-2 Ca0·1r0y+1Ca0·1r0y nomequilibrium 900-20,950-120 1150-2 Ca0·1r0y+1Ca0·1r0y nomequilibrium 900-20,950-120 1175-2 Ca0·1r0y+1c nomequilibrium 900-20,950-120 1175-2 Ca0·1r0y+1c nomequilibrium 900-20,950-120 1175-2 Ca0·1r0y+1c nomequilibrium 900-20,950-120 1175-2 Ca0·1r0y+1c nomequilibrium 900-20,950-120 1000-2 1200-2 Ca0·1r0y+1c nomequilibrium 900-218 1000-19 1200-2 Ca0·1r0y+1c </td <td></td> <td>900-3</td> <td>0,950-120</td> <td>1100-18</td> <td>CaO IrO2+N-CaO IrO2+2CaO IrO2</td> <td>nonequilibrium</td>		900-3	0,950-120	1100-18	CaO IrO2+N-CaO IrO2+2CaO IrO2	nonequilibrium		
800-18,850-18, Trace amount of 2Ga0-1rd, 900-20,950-120 1120-2 Ga0-1rd,2+2Ga0-1rd,2 trace amount of 2Ga0-1rd, 900-20,950-120 900-20,950-120 1130-2 Ga0-1rd,2+2Ga0-1rd,2 trace amount of 2Ga0-1rd, 900-20,950-120 1135-2 Ga0-1rd,2+2Ga0-1rd,2+1r trace amount of 2Ga0-1rd, 900-20,950-120 900-20,950-120 1135-2 Ca0-1rd,2+2Ga0-1rd,2+1r nonequilibrium 900-20,950-120 1150-2 Ca0-1rd,2+2Ga0-1rd,2+1r nonequilibrium 900-20,950-120 1175-2 Ca0-1rd,2+Ga0-1rd,2+1r nonequilibrium 900-20,950-120 1175-2 Ca0-1rd,2+Ga0-1rd,2+1r nonequilibrium 900-20,950-120 1175-2 Ca0-1rd,2+1r- nonequilibrium 900-20,950-120 1175-2 Ca0-1rd,2+1rd nonequilibrium 900-20,950-120 1175-2 Ca0-1rd,2+1rd nonequilibrium 900-20,950-120 1175-2 Ca0-1rd,2+1rd nonequilibrium 900-20,950-120 1175-2 Ca0-1rd,2+1rd nonequilibrium 900-18,850-18, 900-18 NCGO-1rd,2+1rd,2+1rd,0+1rd, nonequilibrium 900-18 1000-2 NCGO-1rd,2+1rd,2+1rd		1300-	2	1100-19	2Ca0.1r0,+1r+Ca0.1r0,	nonequilibrium		
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800-18,850-18, 900-20,950-120 1135-2 Ca0·1r0 ₂ +2Ca0·1r0 ₂ tr nonequilibrius 800-18,850-18, 900-20,950-120 1140-2 Ca0·1r0 ₂ +2Ca0·1r0 ₂ tr nonequilibrius 800-18,850-18, 900-20,950-120 1150-2 2Ca0·1r0 ₂ +Ca0·1r0 ₂ tr nonequilibrius 800-18,850-18, 900-20,950-120 1150-2 2Ca0·1r0 ₂ +1r nonequilibrius 800-18,850-18, 900-20,950-120 1175-2 2Ca0·1r0 ₂ +1r nonequilibrius 800-18,850-18, 900-20,950-120 1200-2 2Ca0·1r0 ₂ +1r nonequilibrius 800-18,850-18, 900-18 1200-2 2Ca0·1r0 ₂ +1r nonequilibrius 900-20,950-120 1200-2 4Ca0·1r0 ₂ +1r0 ₂ nonequilibrius 900-20,950-120 1200-2 4Ca0·1r0 ₂ +1r0 ₂ +4Ca0 nonequilibrius 900-18 1000-2 N-Ca0·1r0 ₂ +1r0 ₂ +4Ca0·1r0 ₂ nonequilibrius 900-18 1000-2 N-Ca0·1r0 ₂ +1r0 ₂ +4Ca0·1r0 ₂ nonequilibrius 1000-20,1000-22 1000-18 1000-10 nonequilibrius 1000-20,1000-22 1080-18 Ca0·1r0 ₂ +1r0 ₂ +4-Ca0·1r0 ₂ nonequilibrius 1000-20,1000-22 1200-2		900-2	0,950-120	1130-2	CaO.IrO2+2CaO.IrO2	trace amount of 2CaO-1rO,		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		800-1	8,850-18,			*		
800-18,850-18, 900-20,950-120 1140-2 Ca0-1r02+2Ca0-1r02tr nonequilibrium 800-18,850-18, 900-20,950-120 1150-2 Ca0-1r02+2Ca0-1r02tr nonequilibrium 800-18,850-18, 900-20,950-120 1175-2 ZCa0-1r02+1r nonequilibrium 900-20,950-120 1175-2 ZCa0-1r02+1r nonequilibrium 900-20,950-120 1175-2 ZCa0-1r02+1r nonequilibrium 900-20,950-120 1175-2 ZCa0-1r02+1r nonequilibrium 900-20,950-120 1200-2 ZCa0-1r02+1r0 nonequilibrium 900-20,950-120 1200-2 ZCa0-1r02+1r02 nonequilibrium 900-20,950-120 1200-2 ZCa0-1r02+1r02 nonequilibrium 1000-18,1000-19 1300-2 Ir+Ca0 nonequilibrium 900-18 1000-20 H-Ca0-1r02+1r02+Ca0-1r02 nonequilibrium 1000-20,1000-22 1000-20 H-Ca0-1r02+1r02+Ca0-1r02 nonequilibrium 1000-20,1000-22 1000-18 Ca0-1r02+1r02+Ca0-1r02 nonequilibrium 1000-20,1000-22 1200-2 ⁶ Ca0-1r02+1r02+Ca0-1r02 <td< td=""><td></td><td>900-2</td><td>0,950-120</td><td>1135-2</td><td>CaO.IrO3+2CaO.ErO3+1r</td><td></td></td<>		900-2	0,950-120	1135-2	CaO.IrO3+2CaO.ErO3+1r			
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900-20,950-120 175-2 2Ca0·ir0 ₂ +ir 800-18,850-120 1200-2 2Ca0·ir0 ₂ +ir 800-18,850-120 1200-2 2Ca0·ir0 ₂ +ir 1000-18,1000-19 1240-2 4Ca0·ir0 ₂ +irca0 1000-18,1000-19 1300-2 Ir+Ca0 900-18 900-18 M-Ca0·ir0 ₂ +irc ₄ 2 nonequilibrium 900-18 1000-20 nonequilibrium nonequilibrium 900-20,900-12 1000-20 M-Ca0·ir0 ₂ +ir0 ₂ +Ca0·ir0 ₂ nonequilibrium 900-18 1000-20 M-Ca0·ir0 ₂ +ir0 ₂ +Ca0·ir0 ₂ nonequilibrium 1000-20,1000-22 1000-20 M-Ca0·ir0 ₂ +ir0 ₂ +Ca0·ir0 ₂ nonequilibrium 1000-20,1000-22 1080-18 ^a Ca0·ir0 ₂ +ir0 ₂ +t-Ca0·ir0 ₂ nonequilibrium 1000-20,1000-22 1200-2 ^a Ca0·ir0 ₂ +ir0 ₂ +t-Ca0·ir0 ₂ nonequilibrium 1000-20,1000-22 1200-2 ^b Ca0·ir0 ₂ +ir0 ₂ +t-Ca0·ir0 ₂ nonequilibrium 1000-20,1000-22 1200-2 ^b Ca0·ir0 ₂ +ir0 ₂ +t-Ca0·ir0 ₂ nonequilibrium 1000-20,1000-22 1200-2 ^b Ca0·ir0 ₂ +ir0 ₂ +t-Ca0·ir0 ₂ nonequilibrium 1000-20,1000-22 1200-2 ^b Ca0·ir0 ₂ +i		800-1	8.850-18.					
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1000-10,100-10,1000-10,1000-12,100 1200-2 2CaO-1rO ₂ +1r 1000-18,1000-19 1240-2 4CaO-1rO ₂ +1r 1000-18,1000-19 1200-2 4CaO-1rO ₂ +1r+CaO 1000-18,1000-19 1300-2 Ir+CaO 900-18 N-CaO-1rO ₂ +1rO ₂ +2aO-1rO ₂ nonequilibrium 900-18 1000-20 N-CaO-1rO ₂ +1rO ₂ +CaO-1rO ₂ nonequilibrium 1000-20 N-CaO-1rO ₂ +1rO ₂ +4-CaO-1rO ₂ nonequilibrium 1000-20,1000-22 1000-20 N-CaO-1rO ₂ +1rO ₂ +4-CaO-1rO ₂ nonequilibrium 1000-20,1000-22 1000-18 CaO-1rO ₂ +1rO ₂ +4-CaO-1rO ₂ nonequilibrium 1000-20,1000-22 1200-2 ⁶ CaO-1rO ₂ +1rO ₂ +4-CaO-1rO ₂ nonequilibrium 1000-20,1000-22 1200-2 ⁶ CaO-1rO ₂ +1rO ₂ +4-CaO-1rO ₂ nonequilibrium 1000-20,1000-22 1200-2 ⁶ CaO-1rO ₂ +1rO ₂ +4-CaO-1rO ₂ nonequilibrium 1000-20,1000-22 1200-2 ⁶ CaO-1rO ₂ +1rO ₂ +4-CaO-1rO ₂ nonequilibrium 1000-20,1000-22 1200-2 ⁶ CaO-1rO ₂ +1rO ₂ +1rO ₂ nonequilibrium 1000-18,1000-19 900-3 1rO ₂ +1rO ₂ +1rO		800-1	8.850-18.		1010 1102.11			
1000-19,1000-19 1240-2 66a0-160_21170_240 1000-19,1000-19 1300-2 1r+CaO 900-18,1000-19 1300-2 1r+CaO 900-18 1050-19,200-170_2 nonequilibrium 900-18 1050-19,24500-170_2 nonequilibrium 900-18 1000-20 H-CaO-170_2+CaO-170_2 nonequilibrium 0 60 1000-20 H-CaO-170_2+CaO-170_2 nonequilibrium 1000-20,1000-22 1005-360 CaO-170_2+170_2+4CaO-170_2 nonequilibrium 1000-20,1000-22 1055-360 CaO-170_2+170_2+4CaO-170_2 trace amount of M-CaO-170 1000-20,1000-22 1050-18 CaO-170_2+170_2+4CaO-170_2 trace amount of M-CaO-170 1000-20,1000-22 1250-20 CaO-170_2+170_2+4CaO-170_2 trace amount of M-CaO-170 1000-20,1000-22 1250-20 CaO-170_2+170_2+4CaO-170_2 nonequilibrium 1000-20,1000-22 1250-20 CaO-170_2+170_2+4CaO-170_2 nonequilibrium 1000-20,1000-22 1250-20 CaO-170_2+170_2+4CaO-170_2 nonequilibrium 1000-20,1000-12 1250-20 CaO-170_2+170_2+170_2		900-2	2,950-120	1200-2	2Ca0-1r0_+1r			
1000-18, 1000-19 1000-1 5 55 900-18 N-Ca0·Ir0_2+Ir0_2+Ca0·Ir0_2 nonequilibrium 900-18 1000-20 N-Ca0·Ir0_2+Ir0_2+Ca0·Ir0_2 nonequilibrium 0 60 1000-20 N-Ca0·Ir0_2+Ir0_2+Ca0·Ir0_2 nonequilibrium 1000-20 1000-20 N-Ca0·Ir0_2+Ir0_2+Ca0·Ir0_2 nonequilibrium 1000-20 1000-22 1000-22 N-Ca0·Ir0_2+Ir0_2+Ca0·Ir0_2 rrace amount of N-Ca0·Ir0_1+Ir0_2+Ir0_2+Ir0_2 1000-20, 1000-22 1000-20 1000-20+Ir0_2+Ir0_2+Ir0_2+Ir0_2+Ir0_2 nonequilibrium 1000-20, 1000-22 1000-20 ⁻¹⁸ Ca0·Ir0_2+Ir0_2+Ir0_2+Ir0_2 nonequilibrium 1000-20, 1000-22 1200-2 ⁶ Ca0·Ir0_2+Ir0_2+Ir0_2 nonequilibrium 1000-20, 1000-22 1200-2 ⁶ Ca0·Ir0_2+Ir0_2+Ir0_2 nonequilibrium 1000-20, 1000-22 1200-2 ⁶ Ca0·Ir0_2+Ir0_2+Ir0_2 nonequilibrium 1000-20, 1000-22 1200-2 ⁶ Ca0·Ir0_2+Ir0_2 nonequilibrium 1000-20, 1000-12 1200-2 Ca0·Ir0_2+Ir0_2+Ir0_2 nonequilibrium 1000-18, 1000-19 975-2 Ca0·I		1800-	18.1000-19	1240-2	6Ca0-1r0_+1r+Ca0			
5 55 900-18 M-Ca0'IrO2+IrO2+2Ca0'IrO2 nonequilibrium 900-18 1030-192 M-Ca0'IrO2+Ca0'IrO2 nonequilibrium 0 60 1000-20 M-Ca0'IrO2+Ca0'IrO2 nonequilibrium 1000-20,1000-22 1000-20 M-Ca0'IrO2+IrO2+Ca0'IrO2 nonequilibrium 1000-20,1000-22 1000-20 M-Ca0'IrO2+IrO2+Ca0'IrO2 trace amount of M-Ca0'IrO 1000-20,1000-22 1080-18 ² Ca0'IrO2+IrO2+H-Ca0'IrO2 trace amount of M-Ca0'IrO 1000-20,1000-22 1150-20 ² Ca0'IrO2+IrO2+H-Ca0'IrO2 monequilibrium 1000-20,1000-22 1200-2 ⁴ Ca0'IrO2+IrO2+H-Ca0'IrO2 monequilibrium 1000-20,1000-22 1200-2 ⁴ Ca0'IrO2+IrO2+H-Ca0'IrO2 monequilibrium 1000-20,1000-22 1200-2 ⁴ Ca0'IrO2+IrO2 nonequilibrium 1000-18,1000-19 900-3 IrO2+IrO2+IrO2		1000-	18,1000-19	1300-2	Ir+Ca0			
900-18 1030-192 M-Ca0-1rO ₂ +Ca0-1rO ₂ 100-2 900-18 1030-20 M-Ca0-1rO ₂ +Ca0-1rO ₂ 100-2 1000-20 1000-22 M-Ca0-1rO ₂ +Ca0-1rO ₂ 100-2 1000-20 1000-22 1075-360° Ca0-1rO ₂ +1rO ₂ +Ca0-1rO ₂ 100-2 1000-20 1000-22 1080-18° Ca0-1rO ₂ +1rO ₂ +M-Ca0-1rO ₂ 100-2 1000-20 1000-22 1080-18° Ca0-1rO ₂ +1rO ₂ +M-Ca0-1rO ₂ 100-2 1000-20 1000-22 1200-2° Ca0-1rO ₂ +1rO ₂ +M-Ca0-1rO ₂ 100-2 1000-20 1000-22 1200-2° Ca0-1rO ₂ +1rO ₂ +M-Ca0-1rO ₂ 100-2 1000-20 1000-22 1200-2° Ca0-1rO ₂ +1rO ₂ +M-Ca0-1rO ₂ 100-2 1000-20 1000-12 1200-2° Ca0-1rO ₂ +1rO ₂ +M-Ca0-1rO ₂ 100-2 1000-18 1000-19 900-3 1rO ₂ +M-Ca0-1rO ₂ 100-2 1000-18 1000-19 N-Ca0-1rO ₂ +1rO ₂ +M-Ca0-1rO ₂ 100-2 1000-18 1000-19 N-Ca0-1rO ₂ +1rO ₂ +Ca0-1rO ₂ 100-2 1000-18 1000-19 1075-20 Ca0-1rO ₂ +1rO ₂ +Ca0-1rO ₂ 100-2 1000-18 1000-19 1075-120° Ca0-1rO ₂ +1rO ₂ +Ca0-1rO ₂ 100-2 1000-18 1000-19 1075-120° Ca0-1rO ₂ +1rO ₂ +Ca0-1rO ₂ 100-2 1000-18 1000-19 1075-20 Ca0-1rO ₂ +1rO ₂ +Ca0-1rO ₂ 100-2 1000-18 1000-19 1075-20 Ca0-1rO ₂ +1rO ₂ +Ca0-1rO ₂ 100-2 1000-18 1000-19 1075-20 Ca0-1rO ₂ +1rO ₂ +Ca0-1rO ₂ 100-2 1000-18 1000-19 1075-20 Ca0-1rO ₂ +1rO ₂ +Ca0-1rO ₂ 100-2 1000-18 1000-19 1075-20 Ca0-1rO ₂ +1rO ₂ +Ca0-1rO ₂ 100-2 1000-18 1000-19 1075-20 Ca0-1rO ₂ +1rO ₂ +Ca0-1rO ₂ 100-2 1000-18 1000-19 1075-20 Ca0-1rO ₂ +1rO ₂ +Ca0-1rO ₂ 100-2 1000-18 100-19 100-2 1000-18 100-19 100-2 1000-18 100-19 100-2 1000-18 1000-19 100-2 1000-18 100-2 1000-18 100-2 1000-18 100-2	5			900-18	H-CeO·IrO ₄ +IrO ₄ +2CaO·IrO ₅	nonequilibrium		
1000-10 1000-20 <	-	900-7	8	1050-192	M-CaO·IrO-+CaO·IrO-	nonequilibrium		
10 10<	0		-	1000-20	H-Ca0+Ir0+1r0+Ca0+Ir0-	nonequilibrium		
1000-70 1000-72 <t< td=""><td>•</td><td>1000-</td><td>70</td><td>1001-22</td><td>M=C+0-170-+170-+C+0-170-</td><td>nonequilibrium</td></t<>	•	1000-	70	1001-22	M=C+0-170-+170-+C+0-170-	nonequilibrium		
1000-10,1000-12 1000-20,2000-20 1000-20,2000-20 1000-20,2000-20 1000-20,2000-20 1000-20,2000-20 1000-20,2000-20 1000-20,2000-20 1000-20,2000-20 1000-20,2000-20 1000-20,2000-20 1000-20,2000-20 1000-20,20		1000	70 1000-72	1075-160	C=0.1-0 +1=0 +1-C=0.1=0	trace amount of M-Calling		
1000-20,1000-22 1000-18 Ca0 : Iroy+H-Ca0 : Iroy+H-Ca0 : Iroy nonequilibrium 1000-20,1000-22 1150-20° Ca0 : Iroy+H-Ca0 : Iroy nonequilibrium 1000-20,1000-22 1200-2° Ca0 : Iroy+H-Ca0 : Iroy nonequilibrium 1000-18,1000-19 900-3 Iroy+H-Ca0 : Iroy nonequilibrium 1000-18 1000-18 Iroy+H-Ca0 : Iroy nonequilibrium 1000-18,1000-19 1075-20 Ca0 : Iroy+H-Ca0 : Iroy nonequilibrium 1000-18,1000-19 1070-2 Iroy+H-Ca0 : Iroy nonequilibrium 900-18 Iroy+H-Ca0 : Iroy nonequilibrium <		1000	20,1000-22	1073-300		crace another of method frog		
1000-20 1200-20 <t< td=""><td></td><td>1000-</td><td>20,1000-22</td><td>1150-205</td><td>Call 1102 TH-Call 1102 TE02</td><td>trace encurt of M.C.A.Ivo</td></t<>		1000-	20,1000-22	1150-205	Call 1102 TH-Call 1102 TE02	trace encurt of M.C.A.Ivo		
1000-20,1000-22 1200-2 1200-2 1200-20 4Ca0:1C0_2+TrC2+M-40:1C0_2 nonequilibrium 5 75 1000-18,1000-19 900-3 1C0_2+TrC2+TrC2+Ca0:1C0_2 nonequilibrium 1000-18,1000-19 975-52 H-Ca0:1C0_2+TrC2+Ca0:1C0_2 nonequilibrium 1000-18 1000-18 1C0_2+H-Ca0:1C0_2 nonequilibrium 1000-18 1000-10 M-Ca0:1C0_2+TrC2+Ca0:1C0_2 nonequilibrium 1000-18,1000-19 1075-20 Ca0:1C0_2+TrC2+TrC2 nonequilibrium 1000-18,1000-19 1075-20 Ca0:1C0_2+TrC2 nonequilibrium 1000-18,1000-19 1075-20 Ca0:1C0_2+TrC2 nonequilibrium 1000-18,1000-19 1075-20 Ca0:1C0_2+TrC2 nonequilibrium 1000-18,1000-19 1075-20 Ca0:1C0_2+TrC2 nonequilibrium 000-18,1000-19 1070-2 TrC2+TrC2 nonequilibrium 900-18 1C0_2+H-Ca0:1C0_2 nonequilibrium 975-240 1C0_2+H-Ca0:1C0_2+Ca0:TrC2_ nonequilibrium 900-18 1C0_2+H-Ca0:1C0_2 nonequilibrium 900-18		1000-	20,1000-22	1200 20	Call Ind the second of the second of the second sec	state amount of A-Cavitro		
1000-10, 1000-72 1200-70 c200'1702+174500 nonequilibrium 5 75 1000-18, 1000-19 900-3 1702+17022+1502 nonequilibrium 1000-18 1000-19 1702+1702+1502 nonequilibrium 1000-18 1000-19 175-20 C40'1702+1702 nonequilibrium 1000-18, 1000-19 175-20 C40'1702+1702 1000-18, 1000-19 175-120 ⁵ C40'1702+170 1000-18, 1000-19 175-120 ⁵ C40'1702+170 1000-18, 1000-19 170-2 17620 0 80 900-3 1702+1702 nonequilibrium 900-18 1702+1702+1702 nonequilibrium 900-18 1702+17-20'1702+1702 nonequilibrium 975-240 1702+17-20'1702+1702 nonequilibrium 975-240 1702+17-20'1702+1702 nonequilibrium 975-240 1702+17-20'1702+1702 nonequilibrium 1000-4 1702+17-20'1702+1702 nonequilibrium		7000-	1000-22	1200-2-	Cauring the state	waaequiliorium		
5 75 1000-18,1000-19 900-3 Lr03+H-CBO·IF02 nonequilibrium 975-52 H-CBO·IF02+E702+E702+E702+E702 nonequilibrium 1000-18 1000-18 1702+H-CBO·IF02 nonequilibrium 1000-18 1000-19 K-CBO·IF02+E702+E702+E702+E702 nonequilibrium 1000-18,1000-19 1075-120 ^C CBO·IF02+IF02+IF02 nonequilibrium 1000-18,1000-19 1075-120 ^C CBO·IF02+IF02 nonequilibrium 1000-18,1000-19 1075-120 ^C CBO·IF02+IF02 nonequilibrium 1000-18,1000-19 1075-120 ^C CBO·IF02+IF02 nonequilibrium 1000-18,1000-19 1070-2 IF102+H-CBO·IF02 nonequilibrium 000-18,1000-19 1000-2 IF40-H-CBO·IF02 nonequilibrium 900-18 IF02+H-CBO·IF02 nonequilibrium 975-240 IF02+H-CBO·IF02 nonequilibrium 975-240 IF02+H-CBO·IF02 nonequilibrium 900-18 1000-4 IF02+H-CBO·IF02 nonequilibrium 900-18 1000-4-4 IF02+H-CBO·IF02 nonequilibrium <td></td> <td>1000-</td> <td>1000-12</td> <td>1230-20</td> <td>4CaU-1102+114C80</td> <td>unuednitiolinu</td>		1000-	1000-12	1230-20	4CaU-1102+114C80	unuednitiolinu		
975-52 8.4Ca0.ir0 ₂ +ir0 ₂ +Ca0.ir0 ₂ nonequilibrium 1000-18 1000-19 1000-102, 1000+102, 1000-102, 1000+102, 1000-102, 1000-103, 1000-19 1075-20 Ca0.ir0 ₂ +ir0 ₂ +Ca0.ir0 ₂ +ir0 nonequilibrium 1000-18, 1000-19 1075-20 Ca0.ir0 ₂ +ir0 ₂ +Ca0.ir0 ₂ +ir0 nonequilibrium 1000-18, 1000-19 1075-20 Ca0.ir0 ₂ +ir0 ₂ +ir0 ₂ 1000-18, 1000-19 1075-120 Ca0.ir0 ₂ +ir0 ₂ 1000-18, 1000-19 100-2 ir+Ca0.ir0 ₂ nonequilibrium 900-18 ir0 ₂ +irCa0.ir0 ₂ +Ca0.ir0 ₂ nonequilibrium 975-24 ir0 ₂ +irCa0.ir0 ₂ nonequilibrium 1000-4 ir0 ₂ +irCa0.ir0 ₂ nonequilibrium 1000-4 ir0 ₂ +irCa0.ir0 ₂ nonequilibrium	5	1000-	18,1000-19	900-3	2r02+H-Ca0-Ir02	nonequilibrium		
1000-18 Ir02+H-Ca0·IrO2 nonequilibrium 1000-18 1000-19 N-Ga0·IrO2+IrO2+Ca0·IrO2 nonequilibrium 1000-18,1000-19 1075-20 Ca0·IrO2+IrO2+IrO nonequilibrium 1000-18,1000-19 1075-20 Ca0·IrO2+IrO2 nonequilibrium 1000-18,1000-19 1075-120 ⁶ Ca0·IrO2+IrO2 nonequilibrium 1000-18,1000-19 1000-7 Ir+Ca0·IrO2 nonequilibrium 00 80 900-3 IrO2+H-Ca0·IrO2 nonequilibrium 900-18 IrO2+H-Ca0·IrO2 nonequilibrium 001-14 900-18 IrO2+H-Ca0·IrO2 nonequilibrium 900-18 IrO2+H-Ca0·IrO2 nonequilibrium 000-4 IrO2+H-Ca0·IrO2 nonequilibrium 000-4 IrO2+H-Ca0·IrO2 nonequilibrium <td></td> <td></td> <td></td> <td>975-52</td> <td>M-Ca0-Ir02+Ir02+Ca0-Ir02</td> <td>nonequilibrium</td>				975-52	M-Ca0-Ir02+Ir02+Ca0-Ir02	nonequilibrium		
1000-18 1000-19 M-Ca0:1r02+1r02+Ca0:1r02 nonequilibrium 1000-18,1000-19 1075-20 Ca0:1r02+1r02 nonequilibrium 1000-18,1000-19 1075-20 Ca0:1r02+1r02 nonequilibrium 1000-18,1000-19 1075-20 Ca0:1r02+1r02 nonequilibrium 1000-18,1000-19 1075-20 Ir4Ca0:1r02+1r02 nonequilibrium 0 80 900-3 1r02+M-Ca0:1r02+Ca0:1r02 nonequilibrium 900-18 1r02+M-Ca0:1r02+Ca0:1r02 nonequilibrium nonequilibrium 900-18 1r02+M-Ca0:1r02+Ca0:1r02 nonequilibrium nonequilibrium 900-18 1r02+M-Ca0:1r02+Ca0:1r02 nonequilibrium nonequilibrium 900-18 1000-4 1r02+M-Ca0:1r02 nonequilibrium				1000-18	Ir02+M-Ca0.Ir02	nonequilibrium		
1000-18,1000-19 1075-20 Cmio Tr02+H-Cmio Tr02+Tr nonequilibrium 1000-18,1000-19 1075-120 ⁶ Cmio Tr02+Tr02 nonequilibrium 1000-18,1000-19 1000-2 t+4Cmio nonequilibrium 0 90 900-3 1r02+H-Cmio Tr02 nonequilibrium 975-240 1702+H-Cmio Tr02 nonequilibrium 975-240 1702+H-Cmio Tr02 nonequilibrium 1000-4 1r02+H-Cmio Tr02 nonequilibrium 1000-4 1r02+H-Cmio Tr02 nonequilibrium 1000-4 1r02+H-Cmio Tr02 nonequilibrium		1000-	18	1000-19	M-Ca0·Ir02+Ir02+Ca0·Ir02	nonequilibrium		
1000-18,1000-19 1075-120 ⁶ Ca0·TrO ₂ +1rO ₂ 1000-18,1000-19 1300-2 I++Ca0 0 90 900-3 IrO ₂ +N-Ca0·TrO ₂ nonequilibrium 900-18 IrO ₂ +N-Ca0·TrO ₂ +Ca0·TrO ₂ nonequilibrium 975-240 IrO ₂ +N-Ca0·TrO ₂ nonequilibrium 1000-4 IrO ₂ +N-Ca0·TrO ₂ nonequilibrium 1000-4 IrO ₂ +N-Ca0·TrO ₂ nonequilibrium 1000-4 IrO ₂ +N-Ca0·TrO ₂ nonequilibrium		1000-	18,1000-19	1075-20	CaO.IrO2+H-CaO.IrO2+Ir	nonequilibrium		
1000-18,1000-19 1300-2 Ir+Ca0 0 80 900-3 1r0 ₂ +H-Ca0'IrO ₂ nonequilibrium 900-18 1r0 ₂ +H-Ca0'IrO ₂ +Ca0'IrO ₂ nonequilibrium 975-240 1r0 ₂ +H-Ca0'IrO ₂ +Ca0'IrO ₂ nonequilibrium 1000-4 1r0 ₂ +H-Ca0'IrO ₂ +Ca0'IrO ₂ nonequilibrium 900-18 100-4 1r0 ₂ +H-Ca0'IrO ₂ +T0+Tr sonequilibrium		1000-	18,1000-19	1075-120 ^C	Ca0'Ir02+Ir05			
0 80 900-3 1702+K-CaO'1702 nonequilibrium 900-18 1702+K-CaO'1702+CaO'1702 nonequilibrium 975-240 1702+K-CaO'1702+CaO'1702 nonequilibrium 1000-4 1702+K-CaO'1702+CaO'1702+Tr sonequilibrium		1000-	18,1000-19	1300-2	Er+Ca0			
900-18 Ir0 ₂ +H-GaO·Ir0 ₂ +GaO·Ir0 ₂ nonequilibrium 975-240 Ir0 ₂ +H-GaO·Ir0 ₂ +GaO·Ir0 ₂ nonequilibrium 1000-4 Ir0 ₂ +H-GaO·Ir0 ₂ nonequilibrium	0			900-3	1r0 ₂ +H-CaO·Ir0 ₂	nonequilibrium		
975-240 1r0 ₂ +H-Cg0·1r0 ₂ +C ₄ 0·1r0 ₂ nonequilibrium 1000-4 1r0 ₂ +H-Cg0·1r0 ₂ nonequilibrium 900-1A 1010-4 H-Cg0·1r0 ₂ +Cr exceedilibrium				900-18	Ir0,+H-CaO-Ir0,+CaO.Ir0,	nonequilibrium		
1000-4 Ir0_H-Ce0-Ir0_ nonequilibrium				975-240	1r03+H-Ca0.1r03+Ct0.1r03	nonequilibrium		
900-18 1030-6 H-Ca0-Ir0.+Ir monenullibrium				1000-4	IrO ₂ +M-CeO·IrO ₂	nonequilibrium		
		900-1		1030-4	H-CaO·IrO.++CaO·IrO.++Ir	nonequilibrium		
900-18.1300-2 1075-19 Ir+Ca0-1r0_+2Ca0-1r0_ Ca0-1r0_ from ir+		900-1	-	1075-19	Iv+Ca0-1r0_+2Ca0-Ir0_	Ca0.1r0, formed from ir+Ca0		
900-18 1135-4 N-CaO·iro.+CaO·iro.+Ir nonenuilibrim		900-1	-,	1175-4	M-CaO·IrO.+CaO·IrO.+Ir	nonequilibrium		
900-18 1200-21 4Ca0-Fr0.4Fr		900-1	-	1200-21	4Ca0-Ir0-+Ir			
200-18 1300-2 Twite-0		900-1		1200-2	Test = 0			

 All specimens wars heat treated in open platinum tubes and air quenched unless otherwise indicated. All temperatures listed applied to (IPTS 1968).

b Phases identified are given in order of the relative amount present at room temperature; N-CaO'IrO₂ = metastable CaO'IrO₂ probably a metastable phase in air at atmospheric pressure.

c Sealed platinum tube container; quenched in ice water.

d Open gold tube container; sir quenched.

a No entry under "Previous" column indicates the specimen received no prior heat treatment.

Tables II and III list the indexed X-ray powder patterns for each binary phase in the CaO-IrO₂ system. Dissociation temperatures of the stable phases are indicated by Fig. 1.

This system is somewhat similar to the $SrO-IrO_2$ system (1) since both systems have three stable compounds (4:1, 2:1, 1:1) in air. The 4:1 compounds of both systems have hexagonal (rhombo-

THE CaO-IrO2-Ir SYSTEM

Table	11.
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X-Ray Diffraction Powder Data for 4CaO.IrO2 and 2CaO.IrO2

		(CuKα rad	liation) ^a				
4Ca0	Ir02 ^b		2Ca0.Ir02 ^c				
d((Å)		d(Å)				
obs	calc	1/11	hk1	obs	calc	1/11	
4.667 4.612 3.282 2.921	4.665 4.610 3.279 2.919	71 73 42 21	110 200 001 210	4.709 4.079 3.193 3.083	4.710 4.079 3.195 3.084	100 4 10 2	
2.693 2.682 2.652 2.3323 2.3053 2.1980	2.693 2.683 2.652 2.3326 2.3052 2.1977	100 23 53 19 61 16	300 111 220 310 211 301	2.718 2.643 2.355 2.262 2.217 2.071	2.720 2.644 2.355 2.263 2.219 2.071	67 86 22 2 8 15	
2.0818 2.0669 1.9791 1.9012 1.7634	2.0814 2.0667 1.9795 1.9008 1.7633	65 79 41 25 49	400 221 320 410 321	2.0395 1.8960 1.8714 1.7804 1.6148	2.0397 1.8958 1.8718 1.7804 1.6150	3 36 3 16 2	
1.7509 1.7367 1.6394 1.5948 1.5549	1.7513 1.7368 1.6396 1.5951 1.5550	29 47 8 8 40	002 330 411 112 331	1.5981 1.5701 1.5556 1.5130 1.4095	1.5975 1.5702 1.5552 1.5129 1.4092	8 12 34 10 8	
1,5466 1,4735 1,4599 1,4052 1,4009	1.5469 1.4734 1.4596 1.4050 1.4005	48 18 21 9 19	302 600 222 520 601	1.3773 1.3601 1.3222 1.3064 1.2511	1.3774 1.3598 1.3221 1.3065 1.2512	11 6 5 5 3	
1.3828 1.3469 1.3416 1.3259 1.3043	1.3830 1.3468 1.3413 1.3258 1.3043	10 22 22 19 2	521 412 332 441 710	1.2095 1.1892 1.1199 1.1049 1.0808	1.2093 1.1890 1.1198 1.1050 1.0807	8 6 4 3 3	
1.2937 1.2928 1.2893 1.2833 1.2756	1.2938 1.2926 1.2891 1.2833 1.2753	12 11 13 29 10	113 602 630 711 522	1.0389 1.0357 1.0280 1.0237 1.0114	1.0388 1.0355 1.0279 1.0237 1.0113	3 4 5 3	
1.2036 1.2009 1.1898 1.1529 1.1308	1.2035 1.2007 1.1895 1.1526 1.1306	9 10 5 3 2	631 223 413	0.9785 0.9704 0.9140	0.9785 0.9704 0.9140	3 3 4	
1.1285 1.1192 1.1124 1.0704 1.0678	1.1283 1.1189 1.1121 1.0702 1.0675	5 8 3 2 25					
1.0410 1.0338 1.0184 1.0093	1.0406 1.0333 1.0184 1.0089	4 3 6 2					
	4Ca0. obs 4.667 4.612 3.282 2.921 2.693 2.682 2.3323 2.3053 2.3053 2.0669 1.9012 1.7634 1.7634 1.7634 1.7509 1.7367 1.6394 1.7367 1.6394 1.7367 1.6394 1.7549 1.7367 1.6394 1.7367 1.6394 1.7549 1.4599 1.4599 1.4599 1.4599 1.4009 1.3828 1.3259 1.3043 1.2937 1.2938 1.2931 1.2937 1.2938 1.2931 1.2937 1.2938 1.2931 1.2937 1.2938 1.2931 1.2937 1.2938 1.2069 1.3043 1.2937 1.2938 1.2036 1.2037 1.2036 1.2036 1.2036 1.2036 1.2036 1.2037 1.2036 1.2036 1.2036 1.2037 1.2036 1.2036 1.2036 1.2037 1.2036 1.2036 1.2036 1.2037 1.2036 1.2036 1.2036 1.2036 1.2037 1.2036 1.2036 1.2037 1.2036 1.2037 1.2036 1.2037 1.2036 1.2037 1.2036 1.2037 1.2036 1.2037 1.2036 1.2037 1.2036 1.2037 1.2036 1.2037 1.2036 1.2037 1.2041 1.0041 1.0041 1.0043 1.0043 1.0044	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c cut \alpha & rad} \hline (Cut \alpha & rad} \hline 4 Ca0 \cdot Ir0_2^{b} \\ \hline \hline d($ $ $ $ $ $ calc $ $ $ $ $ $ $ $ $ $ $ $ $ $ $ $ $ $ $$	$\begin{array}{c ccutca radiation)^a} \hline \hline$	$\begin{array}{c cutx} \operatorname{radiation}^{4} \\ \hline \\ $	$\begin{array}{c cutx} radiation)^{d} \\ \hline \\ $	

^a d-interplanar spacing, I/I₁ - relative intensity

b X-ray pattern obtained from specimen heat treated at 1230°C for 2 hrs. Indexing based on hexagonal cell with a=9.330 and c=11.228Å.

^c X-ray pattern obtained from specimen treated at 1075° for 20 hrs. Indexing based on hexagonal cell with a=9.421 and c=3.195Å.

hedral) symmetry, and appear similar in structure. The 4SrO·IrO₂ has been reported to have the K₄CdCl₆-type structure (5). By analogy the X-ray pattern of 4CaO·IrO₂ was indexed with a hexagonal (rhombohedral) cell, a = 9.330 Å and c = 11.228 Å. However, the 2:1 and 1:1 compounds in the present system differ in symmetry and have no apparent similarity to the corresponding stable compounds in the SrO-IrO₂ system. Babel, Rudorff, and Tschopp (6) reported a hexagonal structure for 2CaO·IrO₂. Our hexagonal cell with a = 9.421 Å and c = 3.195 Å, is in good agreement. A structure for CaO·IrO₂ (1:1) was proposed by Rodi and Babel (7). Our orthorhombic cell with a = 3.145 Å, b = 9.857 Å, and c = 7.296 Å, is essentially the same.

We detected a phase that appears to be a metastable CaO·IrO₂ (M-1:1) compound³ in air. It exists from about 900 to 1100°C, always in combination with other phases, usually the stable 1:1 compound. All attempts to produce a single phase were unsuccessful. Table III gives powder X-ray ³ This composition yielded the greatest quantity of the phase.

Table	III.
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X-Ray Diffraction Powder Data for CaO.IrO2 and Metastable CaO.IrO2

			(CuKa rad	iation) ^a					
	Ca0+1	Ir02 ^b	Metastable CaO·IrO2 ^c						
d(Å)					d(Å)				
hkl	obs	calc	1/11	hkl	obs	calc	1/1		
020 002 110 031 022	4.927 3.645 2.994 2.930	4.928 3.648 2.996 2.996 2.932	69 44 56 100	101 020 111 002 121	3.860 3.832 3.449 2.792 2.721	3.863 3.836 3.450 2.793 2.722	78 43 25 100		
111 040 112 130 131	2.771 2.464 2.314 2.271 2.1691	2.771 2.464 2.315 2.272 2.1691	3 24 41 41 9	200 022 220 202 040	2.673 2.259 2.193 1.932 1.918	2.673 2.258 2.193 1.931 1.918	24 10 8 30 15		
042 132 113 004 024	2.0417 1.9286 1.8886 1.8237 1.7105	2.0420 1.9285 1.8882 1.8240 1.7106	12 41 46 16	103 222 141 301 123	1.758 1.725 1.718 1.6978 1.5983	1.759 1.725 1.718 1.6978 1.5986	8 14 16 6 12		
150 060 200 114 211 152	1.6704 1.6426 1.5720 1.5578 1.5190	1.6703 1.6428 1.5724 1.5580 1.5187 1.5187	13 3 10 19 20	042 321 142 213 242	1.5808 1.5530 1.5170 1.4979 1.3613	1.5811 1.5525 1.5162 1.4985 1.3609	8 19 3 2 8		
220 } 062 } 044 202 134	1.4984 1.4665 1.4443 1.4227	1.4980) 1.4980) 1.4661 1.4440 1.4223	18 11 5 13	143 341 224	1.2965 1.2714 1.1779	1.2962 1.2712 1.1781	4 3 3		
222 240 170 242 0 80	1.3857 1.3258 1.2856 1.2460 1.2324	1.3857 1.3255 1.2852 1.2458 1.2321	14 5 3 9						
251 204 026 082 224	1.2126 1.1911 1.1808 1.1677 1.1579	1.2122 1.1909 1.1806 1.1673 1.1576	6 4 5 3 3						
116 065 262 244 174	1.1269 1.0910 1.0847 1.0725 1.0508	1.1267 1.0910 1.0846 1.0723 1.0506	5 2 6 8 3						
056 084	1.0349	1.0349	2 3						

^a d-interplanar spacing, I/I_1 - relative intensity.

b X-ray pattern obtained from specimen heat treated at 950°C for 120 hrs. Indexing based on orthorhombic cell with a=3.145, b=9.857, and c=7.296 Å.

^C X-ray pattern obtained from specimen heat treated at 950°C for 2 hrs. Indexing based on orthorhombic cell with a=5.346, b=7.672, and c=5.587Å.

diffraction data for the M-1:1 compound indexed as an orthorhombic perovskite cell with a = 5.346 Å, b = 7.672 Å, and c = 5.587 Å. It appears to be similar to other orthorhombic perovskites like CaO·TiO₂ (8) and high pressure SrO·IrO₂ (9).

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