ASPECTS OF THE CHEMISTRY OF SOME STONY METEORITES

by

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Thesis submitted in fulfilment of the requirements
for the degree of Master of Science in the University
of Cape Town

Department of Geochemistry
University of Cape Town
May 1971

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to Professor L.H.Ahrens for suggesting this research project, and to both Professor Ahrens and Mr. A.J.Erlank for guidance and fruitful discussion during its course.

Many members of the Department of Geochemistry assisted the author in one respect or another. In particular, Messrs J.P.Willis, E.J.D.Kable, H.Fesq and Dr. J.J. Gurney advised and assisted the author in regard to the use of the X-ray spectrometers and in data computation. Mr. P.K.Hofmeyr kindly undertook the photographic work, and Mr. W.Hall assisted in various technical aspects of the work. Drs. R.V.Danchin and H.von Michaelis assisted in obtaining meteorite samples. Their contribution is gratefully acknowledged. Mrs. R.E.Tullues assisted with the proof-reading.

The author is grateful to Mr. R.O.Chalmers, Dr. C.B. Moore, Dr. K.K.Turekian, Professor J.Fabries, Dr. J.A. Philpotts, Dr. G.Kurat, Professor G.Rutten, Dr. R.S. Clarke and Dr. C. Frondel for the loan and donation of meteorite samples. In addition, Dr. J.MacIver and Dr. J.Ferguson of the University of the Witwatersrand assisted in obtaining meteorite samples.

Financial assistance from the Council for Scientific and Industrial Research and the Department of Geochemistry is gratefully acknowledged.

The author wishes also to express his gratitude to his wife, Erna, for her assistance with the production of this thesis, and particularly for her patience and understanding during the course of the project.

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Appendix I

Computer programs

Fortran IV programs for use in conjunction with
an IBM 1130 computer

1. Program for the calculation of Zr, Y, Sr and Rb.
2. Program for the calculation of Sr.
3. Program for the calculation of Cr or K.

PROGRAM FOR THE CALCULATION OF Zr, Y, Sr, AND Rb.

```
      REAL INT, INTER, KONK(20,4),MOLY, NPEAK(4), NSPK(20,4) , MO(20)
      INTEGER BLANK,ADDT1,ADDT2,STD,Q
      DIMENSION BLAK(3),BG(5),PK(4),BGUP(4),BGF(4),FACT(4),SBG(20
     *,5),STAND(20,2),SPK(20,4),CONC(20,4), SBGUP(20,4),SL(20,4),BACK
     *(4),SLO(4),ABSE(4),RELER(4),SAMPL(3),PEAK(4),RSD(20) ,
     *ELE(5), DLIM(5)    ,ERR(5)
      IREAD=8
      IWRIT=5
      DT=0.000003
      N=0
      ZRF=0
      SRF=0
      YFA=0
      RBF=0
      INTER=0
      M=0
      L=0
      RATIO=0
      SLZR=0
      SLY=0
      SLSR=0
      SLRB=0
C
C SECTION 1  BACKGROUND CORRECTION FACTORS
C
C             REQUIREMENTS---A SERIES OF BLANKS OF DIFFERENT
C             MASS ABSORPTION COEFFICIENTS MEASURED ON ALL
C             BACKGROUND AND PEAK POSITIONS
C
      WRITE(IWRIT,99)
   99 FORMAT(1H1,26X,'THE DETERMINATION OF ZR, Y, SR AND RB BY X-RAY FLU
     *ORESCENCE ANALYSIS',//,1H ,10X,'FACTORS FOR THE DETERMINATION OF B
     *ACKGROUND UNDER PEAKS',//,1H ,20X,'BLANK',10X,'ZR FACTOR',10X,'Y F
     *ACTOR',10X,'SR FACTOR',10X,'RB FACTOR',//)
      READ(IREAD,100) SFBG,SFPK,TBG,TPK,BLANK,ADDT1,ADDT2,STD
  100 FORMAT(4F4.0,4I4)
C  READS SCALE FACTORS ON BG, PK, TIME ON BG, PK, NO OF BLANKS, NO OF RB
C ADDITIONS, NO OF SR ADDITIONS, AND NO OF STANDARDS
  109 READ(IREAD,101) (BLAK(J),J=1,3),(BG(K),K=1,5),(PK(K),K=1,4)
  101 FORMAT(3A4,9F5.0)
      N=N+1
C READS 5 BACKGROUND POSITIONS, STARTING AT ZR, PLUS PEAKS IN THE ORDER
C ZR,Y,SR,RB, ALL OFF ONE CARD
      DO 102 K=1,5
      BG(K)=BG(K)*SFBG/TBG
  102 BG(K)=BG(K)/(1-BG(K)*DT)
C BACKGROUND POSITIONS ARE DEAD-TIME CORRECTED
      DO 103 K=1,4
      PK(K)=PK(K)*SFPK/TPK
  103 PK(K)=PK(K)/(1-PK(K)*DT)
C PEAK POSITIONS ARE DEAD TIME CORRECTED
      DO 104 K=1,4
      BGUP(K)=BG(K)+BG(K+1)
      FACT(K)=PK(K)/BGUP(K)
```

```
C CALCULATES THE RATIO OF THE BACKGROUND IN THE PEAK POSITION TO THE
C SUM OF THE BACKGROUNDS ON THE SIDES OT THE PEAK
      GO TO (105,106,107,108),K
  105 ZRF=ZRF+FACT(K)
      GO TO 104
  106 YFA=YFA+FACT(K)
      GO TO 104
  107 SRF=SRF+FACT(K)
      GO TO 104
  108 RBF=RBF+FACT(K)
  104 CONTINUE
      WRITE(IWRIT,111) (BLAK(J),J=1,3),(FACT(K),K=1,4)
  111 FORMAT(1H ,13X,3A4,11X,F8.6,10X,F8.6,11X,F8.6,11X,F8.6,/)
      IF(N-BLANK)109,110,109
  110 ZRF=ZRF/BLANK
      YFA=YFA/BLANK
      SRF=SRF/BLANK
      RBF=RBF/BLANK
      BGF(1)=ZRF
      BGF(2)=YFA
      BGF(3)=SRF
      BGF(4)=RBF
C CALCULATES AVERAGE BACKGROUND CORRECTION FACTORS
      WRITE(IWRIT,113) ZRF,YFA,SRF,RBF
  113 FORMAT(1H ,/,6X,'AVERAGE FACTORS ARE',11X,F8.6,10X,F8.6,11X,F8.6,
     *11X,F8.6,////)
C
C SECTION 2  RB INTERFERENCE ON Y
C
C              REQUIREMENTS---BLANKS OF APPROXIMATELY 20PER CENT
C              FE2O3/80PER CENT SIO2 CONTAINING 1500-2500PPM RB
      WRITE(IWRIT,120)
  120 FORMAT(1H ,10X,'CORRECTION FACTORS FOR RB INTERFERENCE ON Y',//,
     *1H ,20X,'RB ADDITION',10X,'CORRECTION FACTOR',/)
  116 READ(IREAD,114) (BLAK(J),J=1,3),(BG(K),K=1,5),Y,RB
  114 FORMAT(3A4,7F5.0)
C READS 5 BACKGROUND POSITIONS PLUS Y AND RB PEAK IN ORDER TO CALCULATE
C THE RB/Y INTERFERENCE FACTOR
      M=M+1
      DO 119 K=1,5
      BG(K)=BG(K)*SFBG/TBG
  119 BG(K)=BG(K)/(1-BG(K)*DT)
C DEAD TIME CORRECTS
      Y=Y*SFPK/TPK
      Y=Y/(1-Y*DT)
      RB=RB*SFPK/TPK
      RB=RB/(1-RB*DT)
C DEAD TIME CORRECTS
      BCY=Y-((BG(2)+BG(3))*BGF(2))
      BCRB=RB-((BG(4)+BG(5))*BGF(4))
C CORRECECTS THE Y AND RB POSITIONS FOR BACKGROUND
      INT=BCY/BCRB
C CALCULATES THR RATIO OF THE Y TO THE RB POSITION
      INTER=INTER+INT
      WRITE(IWRIT,115) (BLAK(J),J=1,3),INT
  115 FORMAT(1H ,19X,3A4,14X,F8.6,/)
      IF (M-ADDT1)116,117,116
  117 RBYF=INTER/ADDT1
C CALCULATES THE AVERAGE Y CORRECTION FACTOR
      BRBYF=RBYF
      WRITE(IWRIT,118)BRBYF
```

```
  118 FORMAT(1H ,//,6X,'AVERAGE FACTOR IS',23X,F8.6,////)
C
C SECTION 3  SR INTERFERENCE ON ZR
C
C              REQUIREMENTS---BLANKS OF APPROXIMATELY 20PER CENT
C              FE2O3/80PER CENT SIO2 CONTAINING 1500-2500PPM SR
      WRITE(IWRIT,121)
  121 FORMAT(1H ,10X,'CORRECTION FACTORS FOR SR INTERFERENCE ON ZR',//,
     *1H ,20X,'SR ADDITION',10X,'CORRECTION FACTOR',//)
  125 READ(IREAD,122) (BLAK(J),J=1,3),(BG(K),K=1,5),ZR,SR
  122 FORMAT(3A4,7F5.0)
C READS 5 BG POSITIONS AND ZR AND SR PEAKS IN ORDER TO CALCULATE THE
C SR/ZR INTERFERENCE CORRECTIONS
      L=L+1
      DO 123 K=1,5
      BG(K)=BG(K)*SFBG/TBG
  123 BG(K)=BG(K)/(1-BG(K)*DT)
C DEAD TIME CORRECTS
      ZR=ZR*SFPK/TPK
      ZR=ZR/(1-ZR*DT)
      SR=SR*SFPK/TPK
      SR=SR/(1-SR*DT)
C DEAD TIME CORRECTS
      BCZR=ZR-((BG(1)+BG(2))*BGF(1))
      BCSR=SR-((BG(3)+BG(4))*BGF(3))
C CORRECTS ZR AND SR PEAKS FOR BACKGROUND
      RAT=BCZR/BCSR
C CALCULATES THE RATIO OF ZR TO SR POSITION
      RATIO=RATIO+RAT
      WRITE(IWRIT,124) (BLAK(J),J=1,3),RAT
  124 FORMAT(1H ,19X,3A4,14X,F8.6,/)
      IF(L-ADDT2) 125,126,125
  126 SRZRF=RATIO/ADDT2
      ASRZR=SRZRF
C CALCULATES AVERAGE ZR CORRECTION FACTOR
      WRITE(IWRIT,127)ASRZR
  127 FORMAT(1H ,//,6X,'AVERAGE FACTOR IS',23X,F8.6,////)
C
C SECTION 4  ZR,Y,SR,RB CALIBRATION CURVES
C
C              REQUIREMENTS---STANDARDS COUNTED IN ALL POSITIONS
C              ABBREVIATIONS--ACONC=ACTUAL CONCENTRATION,MCONC=
C              MEASURED CONCENTRATION, ABERR=ABSOLUTE ERROR,
C              RELER=RELATIVE ERROR
      ZAP=128000.0*DT
      WRITE(IWRIT,128)
  128 FORMAT(1H ,10X,'CALIBRATION CURVES FOR THE DETERMINATION OF ZR, Y,
     * SR AND RB',//,1H ,28X,'ZIRCONIUM',22X,'YTTRIUM',23X,'STRONTIUM',
     *21X,'RUBIDIUM',//,1H ,5X,'SAMPLE',5X,4('ACONC',1X,'MCONC',1X,'ABER
     *R',1X,'RELER',2X))
      DO 139 I=1,STD
      READ(IREAD,130) (STAND(I,J),J=1,2),(SBG(I,K),K=1,5),(SPK(I,K),K=1,
     *4),(CONC(I,K),K=1,4),MO(I)
  130 FORMAT(2A4,13F5.0,F7.0)
C READS STANDARD NAME, FIVE BACKGROUND POSITIONS (STARTING AT ZR END),
C ZR,Y,SR AND RB PEAKS (IN THIS ORDER) AND THE COUNTING TIME IN TNE
C MO POSITION I.E.THE TIME TO ACCUMULATE 128000 COUNTS ON MO COMP.PEAK
      DO 131 K=1,5
      SBG(I,K)=SBG(I,K)*SFBG/TBG
  131 SBG(I,K)=SBG(I,K)/(1-SBG(I,K)*DT)
```

```
C DEAD TIME CORRECTS
      DO 132 K=1,4
      SPK(I,K)=SPK(I,K)*SFPK/TPK
  132 SPK(I,K)=SPK(I,K)/(1-SPK(I,K)*DT)
C DEAD TIME CORRECTS
      MO(I)=MO(I)-ZAP
C DEAD TIME CORRECTS
      DO 133 K=1,4
      SBGUP(I,K)=(SBG(I,K)+SBG(I,K+1))*BGF(K)
  133 NSPK(I,K)=SPK(I,K)-SBGUP(I,K)
C CALCULATES NETT PEAKS FOR STANDARDS
      NSPK(I,1)=NSPK(I,1)-(NSPK(I,3)*SRZRF)
      NSPK(I,2)=NSPK(I,2)-(NSPK(I,4)*RBYF)
C CORRECTS ZR AND Y FOR INTERFERENCE
      DO 134 K=1,4
      SL(I,K)=CONC(I,K)/(MO(I)*NSPK(I,K))
      GO TO ( 135, 136, 137, 138) ,K
  135 SLZR=SLZR+SL(I,K)
      GO TO 134
  136 SLY=SLY+SL(I,K)
      GO TO 134
  137 SLSR=SLSR+SL(I,K)
      GO TO 134
  138 SLRB=SLRB+SL(I,K)
  134 CONTINUE
  139 CONTINUE
      SLZR=SLZR/STD
      SLY=SLY/STD
      SLSR=SLSR/STD
      SLRB=SLRB/STD
      SLO(1)=SLZR
      SLO(2)=SLY
      SLO(3)=SLSR
      SLO(4)=SLRB
C CALCULATES AVERAGE SLOPES OF THE FOUR WORKING CURVES
      DO 142 I=1,STD
      DO 140 K=1,4
      KONK(I,K)=SLO(K)*MO(I)*NSPK(I,K)
      ABSE(K)=CONC(I,K)-KONK(I,K)
  140 RELER(K)=100.0*ABSE(K)/CONC(I,K)
C CALCULATES THE CONCENTRATIONS IN THE STANDARDS USING THE AVERAGE SLOPE
C PLUS THE ABSOLUTE AND RELATIVE ERRORS
      WRITE(IWRIT,141) (STAND(I,J),J=1,2),(CONC(I,K),KONK(I,K),ABSE(K),
     *RELER(K),K=1,4)
  141 FORMAT(1H ,3X,2A4,5X,4(F5.1,1X,F5.1,1X,F5.2,1X,F5.2,2X),/)
  142 CONTINUE
      WRITE(IWRIT,143) SLZR,SLY,SLSR,SLRB
  143 FORMAT(1H ,//,3X,'AVERAGE SLOPES ARE',2X,4(E15.6,7X))
C
C SECTION 5  CALCULATION OF CONCENTRATIONS IN SAMPLES
C
C             ABBREVIATIONS---CO-PPM=CONCENTRATION IN PPM,
C             RSDPPM=RELATIVE STANDARD DEVIATION IN PPM,
C             DLIM-PPM=DETECTION LIMIT IN PPM (3 SIGMA)
  153 WRITE(IWRIT,199)
      Z=0
  199 FORMAT(1H1,26X,'THE DETERMINATION OF ZR, Y, SR, RB BY X-RAY FLUORE
     *SCENCE ANALYSIS',//,1H ,10X,'CONCENTRATIONS IN SAMPLES',//,1H ,9X,
     *'SAMPLE',16X,'ZIRCONIUM',15X,'YTTRIUM',16X,'STRONTIUM',16X,'RUBIDI
     *UM',//,1H ,23X,4('CO-PPM',1X,'RSDPPM',1X,'DLIM-PPM',2X),//)
  152 READ(IREAD,144) (SAMPL(J),J=1,3),(BG(K),K=1,5),(PK(K),K=1,4),MOLY,
```

```
     *Q
  144 FORMAT(3A4,9F5.0,F7.0,I1)
C READS SAMPLE NAME, BACKGROUND POSITIONS STARTING AT THE
C ZR END, FOLLOWED BY PEAKS IN THE ORDER ZR,Y,SR AND RB, AND
C THE MO COMPTON PEAK
      IF(Q-1) 145,200,200
C Q TAKES THE VALUE 0 FOR DATA CARDS AND 1 FOR LAST CARD
  145 DO 146 K=1,5
      BG(K)=BG(K)*SFBG/TBG
  146 BG(K)=BG(K)/(1-BG(K)*DT)
      MOLY=MOLY-ZAP
C DEAD TIME CORRECTS
      DO 147 K=1,4
      PK(K)=PK(K)*SFPK/TPK
  147 PK(K)=PK(K)/(1-PK(K)*DT)
C DEAD TIME CORRECTS
      DO 148 K=1,4
      BGUP(K)=(BG(K)+BG(K+1))*BGF(K)
  148 NPEAK(K)=PK(K)-BGUP(K)
C BACKGROUND CORRECTS PEAKS
      NPEAK(1)=NPEAK(1)-(NPEAK(3)*SRZRF)
      NPEAK(2)=NPEAK(2)-(NPEAK(4)*RBYF)
C CORRECTS FOR ZR AND Y
      DO 149 K=1,4
      ELE(K)=NPEAK(K)*MOLY*SLO(K)
C CALCULATES CONCENTRATION
      PEAK(K)=PK(K)*TPK
      BACK(K)=(BG(K)+BG(K+1))*TBG
      RSD(K)=SQRT(PEAK(K)+BACK(K))/(PEAK(K)-BACK(K))
  149 ERR(K)=ELE(K)*RSD(K)
C CALCULATES COUNTING ERROR
      BGUP(1)=BGUP(1)+(NPEAK(3)*SRZRF)
      BGUP(2)=BGUP(2)+(NPEAK(4)*RBYF)
      DO 150 K=1,4
  150 DLIM(K)=SQRT(BGUP(K)/TPK)*3.0*MOLY*SLO(K)
C CALCULATES DETECTION LIMIT
      WRITE(IWRIT,151) (SAMPL(J),J=1,3),(ELE(K),ERR(K),DLIM(K),K=1,4)
  151 FORMAT(1H ,6X,3A4,4X,4(F6.1,2X,F5.2,2X,F5.2,4X),/)
      Z=Z+1
      IF (Z-26) 152, 153, 153
  200 CALL EXIT
      END
```

PROGRAM FOR THE CALCULATION OF Sr.

```
      REAL MO(20),NPEAK(20),K,MOLY,KONK
      INTEGER SFAB,SFAP,SFAMO
      DIMENSION BGL(10),SR(10),BGH(10),CBGL(10),CSR(10),CBGH(10),BGUP(10
     *),BLANK(10,3),STD(20,3),BG1(20),STR(20),BG2(20),CBG1(20),CBG2(20),
     *CSTR(20),CONC(20),SAMPL(3),SLOPE(20)
      IREAD= 8
      IWRIT= 5
      DT=   0.000003
      SUM=0
      AVSL=0
      TABER=0
      TREL=0
      READ(IREAD,100) SFAB,SFAP,SFAMO,IBLAK,ISTD,TBG,TSR
  100 FORMAT(5I4,2F4.0)
C READS SCALE FACTOR FOR BACKGROUND, SR PEAK AND MO COMPTON PEAK, THE
C NUMBER OF STANDARDS, AND THE COUNTING TIME ON BACKGROUND AND SR PEAK
      WRITE(IWRIT,110)
  110 FORMAT(1H1,32X,'DETERMINATION OF STRONTIUM BY X-RAY FLUORESCENCE
     *ANALYSIS',///,1H ,10X,'BACKGROUND CORRECTION FACTORS AS DETERMINED
     *FROM BLANKS ARE AS FOLLOWS',//,1H ,20X,'BLANK',10X,'FACTOR',/)
      READ(IREAD,101) ((BLANK(I,J),J=1,3),BGL(I),SR(I),BGH(I),I=1,IBLAK)
  101 FORMAT(3A4,3F6.0)
C READS BACKGROUND AND SR PEAK COUNTS ON BLANK SAMPLES
      Q=SFAB/TBG
      R=SFAP/TSR
      DO 103 I=1,IBLAK
      BGL(I)=BGL(I)*Q
      CBGL(I)=BGL(I)/(1-BGL(I)*DT)
      SR(I)=SR(I)*R
      CSR(I)=SR(I)/(1-SR(I)*DT)
      BGH(I)=BGH(I)*Q
      CBGH(I)=BGH(I)/(1-BGH(I)*DT)
C COUNTS ON BLANKS ARE DEAD-TIME CORRECTED
      BGUP(I)=CSR(I)/(CBGH(I)+CBGL(I))
      SUM=SUM+BGUP(I)
      WRITE(IWRIT,104) (BLANK(I,J),J=1,3),BGUP(I)
  104 FORMAT(1H ,16X,3A4,12X,F8.6,/)
  103 CONTINUE
      AVBG=SUM/IBLAK
      FACT=AVBG
      WRITE(IWRIT,105) AVBG
  105 FORMAT(1H ,30X,'AVERAGE BACKGROUND FACTOR IS',3X,F8.6)
C CALCULATES AND WRITES AVERAGE BACKGROUND FACTOR
      READ(IREAD,106) ((STD(I,J),J=1,3),BG1(I),STR(I),BG2(I),MO(I),
     *CONC(I),I=1,ISTD)
  106 FORMAT(3A4,5F6.0)
C READS BG, STRONTIUM AND MO COMPTON PEAK COUNTS AND CONCS FOR STANDARDS
      ZAP=DT*SFAMO*1000.0
      DO 107 I=1,ISTD
      BG1(I)=BG1(I)*Q
      CBG1(I)=BG1(I)/(1-BG1(I)*DT)
      BG2(I)=BG2(I)*Q
      CBG2(I)=BG2(I)/(1-BG2(I)*DT)
      STR(I)=STR(I)*R
      CSTR(I)=STR(I)/(1-STR(I)*DT)
C DEAD TIME CORRECTS STANDARD COUNTS FOR BACKGROUND AND PEAK
      NPEAK(I)=CSTR(I)-((CBG1(I)+CBG2(I))*FACT)
C NETT PEAK FOR STANDARDS CALCULATED
      MO(I)=MO(I)-ZAP
```

```
C DEAD-TIME CORRECTS MO COMPTON PEAK
      SLOPE(I)=CONC(I)/(NPEAK(I)*MO(I))
      AVSL=AVSL+SLOPE(I)
C CALCULATES SLOPE OF CALIBRATION CURVE
  107 CONTINUE
      WRITE(IWRIT,108)
  108 FORMAT(1H ,///,10X,'STRONTIUM WORKING CURVE',//,1H ,20X,'STANDARD'
     *,5X,'ACTUAL CONCENTRATION',5X,'CALCULATED CONCENTRATION',5X,'ABSOL
     *UTE ERROR',5X,'RELATIVE ERROR',/)
      K=AVSL/ISTD
      Z=K
C CALCULATES AVERAGE SLOPE FOR ALL STANDARDS
      DO 112 I=1,ISTD
      X=K*NPEAK(I)*MO(I)
      ABER=CONC(I)-X
      RELER=ABER*100.0/CONC(I)
      TABER=TABER+ABS(ABER)
      TREL=TREL+ABS(RELER)
C CALCULATES CONCENTRATIONS IN STANDARDS FROM THE AVERAGE SLOPE OF THE
C WORKING CURVE, AND EXPRESSES DEVIATIONS IN THE FORM OF ABSOLUTE AND
C RELATIVE ERRORS
      WRITE(IWRIT,109) (STD(I,J),J=1,3),CONC(I),X,ABER,RELER
  109 FORMAT(1H ,18X,3A4,11X,F6.1,20X,F6.1,18X,F6.2, 16X,F7.2,/)
  112 CONTINUE
      AVERA=TABER/ISTD
      AVREL=TREL/ISTD
      WRITE(IWRIT,111) AVERA,AVREL,Z
  111 FORMAT(1H ,/,' AVERAGE ERRORS ARE',72X,F6.2,16X,F7.2,/,1H ,'SLOPE
     *OF CALIBTATION CURVE IS',3X,F8.6)
  150 M=0
      WRITE(IWRIT,130)
  130 FORMAT(1H1,32X,'DETERMINATION OF STRONTIUM BY X-RAY FLUORESCENCE A
     *NALYSIS',////,1H ,10X,'SAMPLE',10X,'CONCENTRATION',10X,'R.S.D.(PPM
     *)',10X,'DET.LIMIT(PPM)',//)
  140 READ(IREAD,113) (SAMPL(J),J=1,3),BCK1,STRN,BCK2,MOLY,L
  113 FORMAT(3A4,4F6.0,I1)
      IF(L-1) 131,141,131
C TEST FOR LAST CARD,WHICH BEARS ONLY A 1 IN COLUMN 37
  131 BCK1=BCK1*Q
      CBCK1=BCK1/(1-BCK1*DT)
      BCK2=BCK2*Q
      CBCK2=BCK2/(1-BCK2*DT)
      STRN=STRN*R
      CSTRN=STRN/(1-STRN*DT)
      MOLY=MOLY-ZAP
C COUNTS FOR SAMPLES ARE DEAD-TIME CORRECTED
      BACK=(CBCK2+CBCK1)*FACT
      PEAK=CSTRN-BACK
      KONK=K*PEAK*MOLY
C CALCULATES CONCENTRATION IN SAMPLE
      DLIM=SQRT(BACK/TSR)*3.0*MOLY*K
      TSRN=CSTRN*TSR
      TBGN=(CBCK1+CBCK2)*TBG
      GAF=TSRN+TBGN
      RSD=SQRT(GAF)/(TSRN-TBGN)
      ERROR=KONK*RSD
C CALCULATES COUNTING STATISTICS
      WRITE(IWRIT,120) (SAMPL(J),J=1,3),KONK,ERROR,DLIM
  120 FORMAT(1H ,7X,3A4,10X,F6.2,15X,F6.3,20X,F6.2,/)
      M=M+1
      IF(M-24) 140,150,140
  141 CALL EXIT
      END
```

PROGRAM FOR THE CALCULATION OF Cr OR K.

```
      REAL NPEAK(20),MU(20),MASP(5),KON(5),NORM,NUM,KONK,NPK,
     *MASS(5),MAS,MUP(20),MUS(20)
      INTEGER Z, P
      DIMENSION BG(5),PK(5),STD(20,3),STAND(5,3),CONC(20),PEAK(20),BACK(
     *20),POS(5),SAMPL(5,3)
      IWRIT=5
      IREAD=8
      P=0
      L=1
      BASE=2000.0
      N=0
      DT=0.0000029
      SDEN=0.0
      SNUM = 0.0
      RELTV = 0.0
      ABSOL = 0.0
      POS(1)=1.0
      POS(2)=0.9914
      POS(3)=0.9828
      POS(4)=0.9981
      POS(5)=1.0
C POSITIONS 1 AND 5 BOTH REFER TO POSITION 1
      READ(IREAD,100) SFBG, SFPK, TBG, TPK
  100 FORMAT(4F4.0)
C READS SCALE FACTOR ON BACKGROUND AND PEAK,PLUS TIME ON BACKGROUND
C AND PEAK,PLUS THE NUMBER OF STANDARDS
      WRITE(IWRIT,200)
  200 FORMAT(1H1,25X,'DETERMINATION OF CHROMIUM/POTASSIUM BY X-RAY FLUOR
     *ESENCE SPECTROMETRY',////)
      WRITE(IWRIT,201)
  201 FORMAT(1H ,10X,'CALIBRATION CURVE',//,20X,'STANDARD',5X,'ACT.CONC'
     *,5X,'MEAS.CONC',5X,'ABS.ERROR',5X,'REL.ERR')
  105 READ(IREAD,101) J
  101 FORMAT(I1)
      IF (J-1) 106,106,107
C J INDICATES THE NUMBER OF READINGS IN EACH SET - I.E. TWO
C REFERENCES PLUS THE INTERVENING SAMPLES. THE LAST STANDARD
C CARD IS INDICATED BY 0 FOR J
  107 DO 103 I=1,J
      READ(IREAD,102) (STAND(I,Z),Z=1,3),BG(I),PK(I),MASP(I),MASS(I),
     *KON(I)
  102 FORMAT(3A4,5F6.0)
      BG(I)=BG(I)*SFBG/TBG
      BG(I)=BG(I)*POS(I)
      BG(I)=BG(I)/(1-BG(I)*DT)
      PK(I)=PK(I)*SFPK/TPK
      PK(I)=PK(I)*POS(I)
      PK(I)=PK(I)/(1-PK(I)*DT)
  103 CONTINUE
      AV=(PK(1)+PK(J))/2.0
      NORM=BASE/AV
      K=J-1
      DO 104 I=2,K
      DO 112 Z=1,3
  112 STD(L,Z)=STAND(I,Z)
      MUP(L)=MASP(I)
      MUS(L)=MASS(I)
      CONC(L)=KON(I)
      PEAK(L)=PK(I)*NORM
      BACK(L)=BG(I)*NORM
      MU(L)=MUP(L)+MUS(L)*1.567
  104 L=L+1
```

```
      GO TO 105
106   L=L-1
      M=L
      DO 401 L=1,M
      NPEAK(L)=PEAK(L)-BACK(L)
      X=NPEAK(L)*MU(L)
      Y=CONC(L)
      NUM=X*Y
      DEN=X*X
      SDEN=SDEN+DEN
      SNUM=SNUM+NUM
401   CONTINUE
      SLOPE=SNUM/SDEN
      DO 109 L=1,M
      KONK=SLOPE*MU(L)*NPEAK(L)
      ABSV=CONC(L)-KONK
      RELER=ABSV*100.0/CONC(L)
      ABSOL=ABSOL+ABS(ABSV)
      RELTV=RELTV+ABS(RELER)
      WRITE(IWRIT,108) (STD(L,Z),Z=1,3),CONC(L),KONK,ABSV,RELER
108   FORMAT(1H ,12X,3A4,8X,F7.1,6X,F7.1,7X,F7.2,6X,F7.2,/)
109   CONTINUE
      GRAD=SLOPE
      ABSOL=ABSOL/M
      RELTV=RELTV/M
      WRITE(IWRIT,110) ABSOL,RELTV,GRAD
110   FORMAT(1H ,12X,'AVERAGE ERRORS',33X,F7.2,6X,F7.2,//,1H ,20X,'SLOPE
     * OF CALIBRATION CURVE',3X,E16.7,////)
204   WRITE(IWRIT,200)
      WRITE(IWRIT,203)
203   FORMAT(1H ,10X,'SAMPLE',5X,'CONCENTRATION',5X,'ERROR(PPM)',5X,'DET
     *.LIM.(PPM)')
298   READ(IREAD,111) J
111   FORMAT(I1)
      P=P+1
      IF (J-1) 300,299,299
299   DO 210 I=1,J
      READ(IREAD,400) (SAMPL(I,M),M=1,3),BG(I),PK(I),MASP(I),MASS(I)
400   FORMAT(3A4,4F6.0)
      BG(I)=BG(I)*SFBG/TBG
      BG(I)=BG(I)*POS(I)
      BG(I)=BG(I)/(1-BG(I)*DT)
      PK(I)=PK(I)*SFPK/TPK
      PK(I)=PK(I)*POS(I)
      PK(I)=PK(I)/(1-PK(I)*DT)
210   CONTINUE
      AV=(PK(1)+PK(J))/2.0
      NORM=BASE/AV
      K=J-1
      DO 211 I=2,K
      BG(I)=BG(I)*NORM
      PK(I)=PK(I)*NORM
      MAS=MASP(I)+MASS(I)*1.567
      NPK=PK(I)-BG(I)
      KONK=NPK*MAS*SLOPE
      DLIM=SQRT(BG(I)/TBG)*3.0*MAS*SLOPE
      ERR= KONK*(SQRT(PK(I)/TPK+BG(I)/TBG))/(PK(I)-BG(I))
      WRITE(IWRIT,212) (SAMPL(I,M),M=1,3),KONK,ERR,DLIM
212   FORMAT(1H ,7X,3A4,5X,F7.1,10X,F7.4,9X,F7.4,/)
211   CONTINUE
      IF (P-26) 298, 204, 204
300   CALL EXIT
      END
```

Appendix II

1. Data used in the construction of Figure 4.
2. Sources, sizes and condition of samples analysed in this work.

Data used in the construction of Figure 4.

Meteorite	%K(fusion)	ppmK(pressed briquette)
Serra de Mage	0.004	-
Stannern	0.050	549
Bereba	0.027	294
Juvinas	0.034	340
Pasamonte	0.030	356
Sioux County	0.027	295
Haraiya	0.025	270
Cachari	0.037	411
Macibini	0.038	399
Malvern	0.034	379
Chaves	0.015	176
Binda	0.006	85
Zmenj	0.014	-
Frankfort (T)	0.007	108
Frankfort (F)	0.011	128
Cumberland Falls	0.017	224
Norton County	0.004	101
Shallowater	0.039	488
Johnstown	0.001	20
Ellemeet	0.001	27
Tatahouine	<0.001	<2
Shalka	<0.001	13
Chassigny	0.022	268
Vigarano	0.029	319
Mokoia	0.028	306
Allende	0.029	300
Leoville	0.009	100
Coolidge	0.010	129
Lancé	0.036	397
Warrenton	0.035	390
Felix	0.034	371

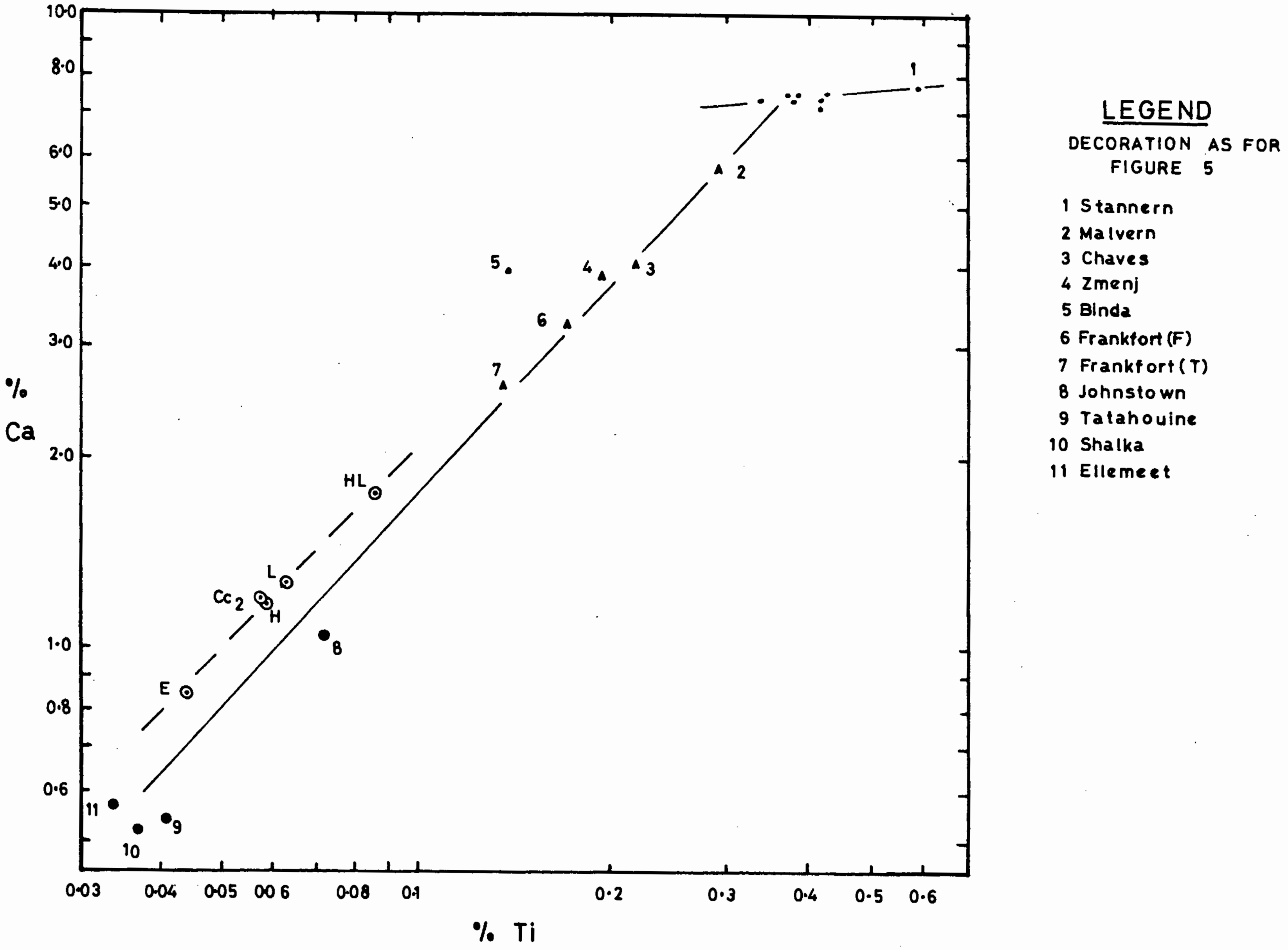
Meteorite	Weight available for analysis	Source	Condition received in.
Allende	29g	SI	single stone
Bereba	9.4g	MNDN	single fragment
Binda	11.4g	AM	small fragments and powder
Cachari	4.9g	MNDN	small fragments
Chassigny	2.1g	MNDN	single fragment
Chaves	4.7g	HU	small fragments
Coolidge	11.4g	SI	slice
Cumberland Falls (achondrite)	5.2g	SI	single fragment
Cumberland Falls (chondrite)	0.6g	SI	single fragment
Ellemeet	20.3g	RU	fragment and powder
Felix	(original 9.2g sample)	UCT	powder
Frankfort(F)	5.3g	HU	small fragments
Frankfort(T)	9.4g	YU	slice
Haraiya	6.7g	ASU	single fragment
Johnstown	(original 21.8g sample)	UCT	powder
Juvinas	10.8g	MNDN	fragments
Lancé	(original 4.6g sample)	UCT	powder
Leoville	8.5g	SI	slice
Macibini	12.2g	SAGS	single fragment
Malvern	(original 4g sample)	UCT	powder
Mokoia	(original 10.2g sample)	UCT	powder
Norton County	(original 10.1g sample)	UCT	powder
Pasamonte	(original 10.7g sample)	UCT	powder
Serra de Mage	(original 10g sample)	NASA	powder
Shalka	(original 9.1g sample)	UCT	powder
Sioux County	(original 10.7g sample)	UCT	powder
Shallowater	6.8g	ASU	slice

Meteorite	Weight available for analysis	Source	Condition received in
Stannern	10.3g	NM	single fragment
Tatahouine	10.0g	MNDN	single fragment
Vigarano	(original 16.3g sample)	UCT	powder
Warrenton	6.2g	HU	small fragments
Zmenj	0.9g	H.B.Wiik	small fragments

Abbreviations:

AM	Australian Museum, Sydney.
ASU	Arizona State University, Tempe.
HU	Harvard University.
MNDN	Museum National D'Histoire Naturelle, Paris.
NASA	National Aeronautics and Space Administration
NM	Naturhistorisches Museum, Vienna.
RU	Rijksuniversiteit te Utrecht, Utrecht.
SAGS	South African Geological Survey, Pretoria.
SI	Smithsonian Institution, Washington.
UCT	University of Cape Town collection.
YU	Yale University.

figure 6



The relationship between Ca and Ti in diogenites, howardites and eucrites. Chondrites are included for comparison.

ABSTRACT

Ten eucrites, four howardites, three enstatite achondrites, eight HL chondrites, the one known chassignite and a chondrite inclusion from the Cumberland Falls achondrite have been analysed for major, minor and some trace elements (viz. Fe, Mn, Ca, Cr, P, Si, Al, Mg, Na, K, Sr, Zr, Y, Ba and Ni) using X-ray fluoresence analysis. A fusion technique was used to determine the more abundant elements, while trace constituents were determined on powdered samples. The data obtained have been critically examined from the point of view of both precision and accuracy, and found to be of a high standard for most elements. Inter-element relationships amongst the diogenites, howardites and eucrites suggest that two distinct processes were involved in the genesis of these meteorites. Theories for the origin of these meteorites have been examined in the light of these inter-element relationships. It is concluded that mixing of diogenitic and eucritic material was responsible for the formation of howardites, while diogenites and eucrites appear to have been formed by processes of igneous differentiation from a single parent magma. The unique achondrite Chassigny may also be a product of this process. Some speculations concerning the composition of the parent material from which these meteorite types crystallized are presented.

The enstatite achondrites are apparently unrelated to the previously mentioned meteorite types. They do, however, show close affinities with the enstatite chondrites . It would appear that the two types are not related by igneous differentiation, but were probably formed by the same processes. The chondrite fragment removed from the Cumberland Falls achondrite has a composition which suggests that it is a member of the genetic sequence represented by enstatite chondrites and achondrites.

The Vigarano and Ornans sub-types of the HL chondrites were observed to exhibit slight but distinct differences in bulk composition, in the form of higher Ca and Al abundances in the Vigarano sub-type. Superimposed on these differences are more dramatic chemical differences which appear to be associated with the recrystallization which some of these meteorites have undergone. These differences include loss of alkali metals, Ca and Al.

INTRODUCTION

At the present time, meteoriticists are employing a great variety of techniques ranging from experimental to petrographic and microprobe studies to study meteorites. In spite of the use of these highly sophisticated methods, the age-old bulk chemical analysis nevertheless still plays a vital role in improving our understanding of the origin of meteorites. Naturally, such analyses must be as true a reflection of the actual meteorite composition as possible. Although this would appear to be axiomatic, it is only in recent years, with the improvement of analytical techniques, that such a situation is being achieved. This has been demonstrated rather dramatically in the case of the Ca/Al ratio in chondrites by Ahrens et al (1968). In view of the difficulties associated with the determination of Al by classical 'wet' techniques, this is perhaps an extreme example, but it nevertheless illustrates thepoint. The implication of the work of Ahrens and his co-workers was that many chondrite, and presumably, achondrite analyses are not as good as might be desired. This is particularly true for older analyses. It was obvious that there was a pressing need for new major element analyses of a representative range of achondrites using an analytical technique which could produce results of a reasonably high standard. This project was aimed at providing this data. Where possible, relatively large samples were sought, so as to ensure representative sampling of the meteorites concerned.

In addition to the above general goal, a more specific aim for this project existed as well. It was apparent from the work of Ahrens et al (1969), Ahrens and von Michaelis (1969a) and of Ahrens (1970 c) that the so-called 'refractory group' of elements (Ahrens 1970a) showed a continuous enrichment from chondrites, through howardites, culminating in eucrites. These elements, typified by Ca and Al were thought to provide a link between the chondrites on the one hand and the howardites and eucrites on the other (Ahrens and von Michaelis 1969b). This aspect needed further investigation, particularly with a view to establishing the presence of any fine structure in the Ca/Al relationship, as it was clearly of some genetic significance. In addition to Ca and Al, however, data for other minor and trace refractory elements on the same powders as those on which the majors were determined were required. The X-ray fluorescence technique used in this laboratory was ideally suited to this purpose.

In addition to studying the enrichment of refractory elements in howardites, investigation of the HL chondrites was undertaken as well, as the few representatives of this group examined by Ahrens and von Michaelis (1969a) showed greater variations in Ca and Al than other chondrite types, and thus were of particular interest as far as the Ca/Al ratio was conerned.

Finally, Ahrens (1970b) had pointed out that the eucrites Stannern and Neuvo Laredo showed slight enrichments of refractory elements relative to other eucrites. A more detailed study of such enrichment~~s~~ trends in eucrites was thus of some interest.

In their investigation of oxygen isotopic relationships in stony meteorites, Taylor et al (1965) had shown that the hypersthene achondrites or diogenites were apparently related to howardites and eucrites. As few recent bulk analyses of members of this group of meteorites had been carried out, some representatives were included in this study.

Enstatite achondrites or aubrites were included as a separate investigation. Earlier theories for achondrite genesis (see, for example, Ringwood 1961 and Mason 1962) had linked these meteorites and diogenites with chondrites by a process of igneous differentiation. It was hoped that a more detailed survey of their chemistry would throw some light on these processes.

SECTION I

SAMPLE PREPARATION PROCEDURE

Introduction.

Classical methods of silicate analysis, even today, seem to be much of an art. Careful scrutiny of comparable data -e.g. lunar samples, indicates the superior quality of the data of some workers compared to that of others. Instrumental methods of silicate analysis are in many respects superior to wet chemical techniques, particularly as they are in no way operator prone (with certain reservations). An important aspect of instrumental analysis is the sample preparation. In addition, the size of the sample used is of some significance. Careful consideration was given to both these aspects.

Sample Size.

In a study of the bulk chemistry of meteorites, one of the most important and most fundamental considerations is that of representative sampling. It is quite clear that if one hopes to deduce processes operative during the formation of meteorites from variations in chemistry, whether major or trace, these variations should be solely due to cosmic processes and not related to poor sampling of the particular meteorite concerned, i.e. the utmost should be done to reduce to a minimum the number of variables determining variation in elemental abundance. This is particularly true where an element occurs in a single phase which is erratically distributed. e.g. Cu (metal) (Moss et al 1967), Cr (in chromite), or Ni (in Kamacite) in some achondrites. Nor is this problem overcome by the use of inter-element ratios. A classical example of this is the Ca/Al ratio in chondrites, howardites and eucrites, which has been shown to vary between very narrow limits (Ahrens and von Michaelis 1969) In howardites and eucrites in particular, it is clear that this ratio is not determined by any one mineral, but rather is controlled by carefully balanced proportions of the Ca bearing phases plagioclase and pyroxene. Variation in the relative proportions of these two minerals is likely to cause variation in the Ca/Al ratio.

There is a disturbing trend amongst meteorite analysts at the present time towards the use of smaller and smaller samples. This has, to an extent, been forced on workers by the desire to conserve material. The dangers involved in this practice have, however, not gone unnoticed. H.B. Wiik had already drawn attention to the problem in 1956 when he observed that metal was extremely sporadically distributed in a large specimen of Norton County he examined. Numerous workers have since referred to the problem. Moore and Brown (1963) for example, found barium to vary extensively in eight different samples of Holbrook.

Because of the wide range in structure amongst meteorites, there cannot be a single, optimum, minimium sample size which would ensure representative sampling. Rather, as suggested by Moss et al (1966), each meteorite should be studied separately, and, after careful examination of as large a fragment as possible, the optimium sample size selected. Thus, they point out that 10 - 15 g samples are often too samll to ensure representative sampling of some meteorites. A similar conclusion was arrived at by Keil (1962), who found that the minimum quantity of sample required to ensure representative sampling varied from 15 g to 70 g, depending on the meteorite.

In their study of the fractionation of elements in chondrites, von Michaelis (1969) and von Michaelis et al (1969) used samples of approximately 10g. The high quality of this data serves to indicate that their sampling was representative. Achondrites, although texturally and minerallogically different from chondrites, are not considered to be fundamentally different from chondrites as far as the problem of sampling is concerned. Therefore, where possible, approximately 10 g samples were sought for this study. Where very small samples were acquired (less than 1 g), every effort was made to ensure that these were representative powders of larger specimens. The actual sample size used may be found in Appendix II. In most cases, the samples studied in this work appear to have been representative, although the two samples of Frankfort analysed showed significant differences from one another. Although the differences between these samples have a significant bearing on the origin of howardites, the fact remains that, in spite of their relatively large size, either one or both were not representative of the meteorite as a whole.

Sample treatment.

Meteorite analysis has traditionally been an extremely difficult undertaking, mainly as a result of the presence of metal, silicate and, in some cases, sulphide phases, and their inherently different physical and chemical properties. The main difficulty arises from the fact that the metal phase cannot be ground to a sufficiently fine state to enable its effective determination by most analytical techniques. Some workers seem to have ignored this problem, e.g. Moss et al (1966). Berry and Rudowski (1965), on the other hand, advocated crushing under liquid air. Von Michaelis et al (1969) used an oxidation technique to homogenize meteorite material after magnetically extracting the metal. In the case of achondrites, these problems are not as acute as in chondrites, since the metal phase is usually a minor constituent of these meteorites. This is also largely true for HL or Type III carbonaceous chondrites, where the metal phase is present only in minor amounts.

The main problem encountered in this work was one of reducing the material to a fine enough state to allow the the analysis of a small aliquot of powder, i.e. metal and silicate had to be completely homogenized, so that the small quantity removed would be representative of the sample as a whole. However, as the metal was found to be at least -60 mesh, the initial crushing procedures were straight forward.

(i) Fusion crust: Every effort was made to remove all traces of fusion crust from samples prior to crushing. Following the technique described by von Michaelis (1969), fusion crusts and any surface stains were removed using an electric engraving tool fitted with a gramaphone needle. The needle was weighed before and after each crust removal. Loss in weight never exceeded 0.2 % (about 0.0003g), indicating negible contamination, particularly as these needles are composed essentially of iron.

(ii) Crushing procedure: The crushing of coarse meteorite fragments was carried out in a 'pitho' steel pestle and mortar. This device had previously been fitted with a rubber sealing ring, to ensure that no loss of fine dust occurred during the crushing process. As the fine material is probably enriched in the softer minerals its loss could lead to a bias in the sample composition.

Tests on the extent of contamination by metal particles flaking off the crushing apparatus were carried out. 0.02% extractable metal was introduced into a test sample of vein quartz, while 0.01% could be extracted from an anorthosite sample. The latter figure probably represents an upper limit as far as this study is concerned, as the meteorites studied here, although of variable hardness, were considerably softer than both quartz and anorthosite, and contamination levels will therefore be appreciably lower. The introduction of these small quantities of steel are unlikely to pose a problem, as 'pitho' steel contains only small quantities of elements other than iron. The limits of the non-ferric components of this steel supplied by the manufacturer are
C 0.9 - 1.0 %, Mn 1.1 - 1.3 %, Cr 0.45 - 0.65 %,
W 0.45 - 0.8 % and V 0.15 % maximum.

Meteorite samples were reduced to -40 mesh in the steel pestle and mortar, and then ground to pass through 60 mesh nylon bolting cloth using a hand agate pestle and mortar. In most cases, all the metal was found to pass through the -60 mesh screen. Where coarser and larger quantities of metal were encountered, an oxidation technique was used for homogenising the samples as described below. The -60 mesh material was then transferred to an agate pestle and mortar, where grinding for one hour reduced the bulk of it to the required mesh size. Samples obtained in powdered form were crushed directly in the agate pestle and mortar to ensure -200 mesh size for the silicate fraction.

Crushing equipment was carefully cleaned with dilute HCl and distilled water between each sample to prevent cross contamination. New nylon bolting cloth was used for each sample. All handling of sample fragments was done with a pair of forceps.

(iii) Estimation of metal: A variety of methods for determining the quantity of metal in a meteorite have been described. These include a chlorine digestion method, as described by Moss et al (1966), $KCuCl_3$, as used by Jarosewich (1966), oxidation by Fe^{3+} (Maynes 1970), NH_4Cl - $HgCl_2$ digestion (Wiik 1956, Easton and Lovering 1963). Point counting has also been used in some instances (e.g. Keil 1968), as has magnetic separation.

As pointed out by Jarosewich (1966), a completely reliable method for metal determination does not exist. The Cl_2 method of Moss et al (1966) is not complete, and magnetic separation of remaining metal has to be undertaken. The magnetic method itself suffers inaccuracy due to entrapped silicate. The effects of the methods employing mercuric and cupric ions on the silicate minerals, and particularly minor minerals is unknown (Jarosewich 1966). As far as this work was concerned, chemical methods had the disadvantage of removing, and, in effect, contaminating the metal phase, and leaving it in a form which is unsuitable to the analytical ~~to the analytical~~ technique used.

In the absence of an accurate and suitable method for the estimation of the small quantities of metal in achondrites, no attempt was made to estimate the metal contents of the meteorites studied in this work.

(iv) Oxidation procedures: In most of the meteorites analysed during this work, the metal was considered to be sufficiently/fine grained so as not to hamper the analytical method to any great extent. In some meteorites, however, the metal was considered to be both too adundant and too coarse to enable treatment as a normal silicate rock. Further homogenization of the samples was essential. For this purpose, the oxidation technique described by von Michaelis et al (1969) and von Michaelis (1969) was used, viz. oxidation of the metal at high temperature in a stream of oxygen and steam. The apparatus used by these workers was slightly modified. The entire apparatus was constructed of glass tubing, fitted with ground-glass joints. In addition, a vitreosil boat was obtained to hold the sample. At intervals during the oxidation, the sample was removed, weighed and ground in an agate pestle and mortar. Oxidation was judged to be complete when no metal particles could be felt under the pestle. Following oxidation, the samples were ground to -200 mesh in an automatic agate pestle and mortar. Von Michaelis (1969) investigated the problem of moisture uptake by the oxidized powder, which could lead to small errors in the factor to reconvert the oxidized to the unoxidized weight. His work showed that this uptake of moisture was sufficiently small to be safely ignored.

(v) Special cleaning procedures: One of the meteorites studied in this work, Frankfort (T), had been impregnated with an oily substance during the manufacture of a thin section. This material made crushing difficult, and sieving impossible. After initial crushing, the sample was immersed in A.R. acetone and placed in an ultrasonic vibrator, which dissolved the offending material completely.

Preparation of samples for analysis.

Two separate methods of X-ray fluorescence were employed in this work, one for the determination of the major and some minor components, which involved dissolving the sample in a flux, and the other for the determination of minor and trace constituents, which involved the use of pressed briquettes of the meteorite powder.

(i) Fusion discs: To overcome the severe matrix effects inherent in X-ray fluorescence analysis for major elements, the fusion technique of Norrish and Hutton (1970) was used. A method of pre-ignition of samples was employed. It is essential that all metal be in an oxidized form during the fusion, as tests indicated that any unoxidized metal would rapidly alloy with the gold-platinum crucible used for the fusions. This would result in low Fe values, particularly for the highly reduced enstatite achondrites, as well as damage to the crucible.

It was therefore necessary to ascertain the optimum pre-heating period required to oxidize all the metal in the samples. Large metal fragments from the chondrite Richardton were heated for 16 hours at 1000°C, the normal pre-heating temperature. After this period, the oxidized fragments were ground to about -200 mesh. No metal was detected during the grinding. X-ray diffraction examination of this powder (Cu tube, 48kV, 20mA, Ni filter, scan. speed 2° 2θ/min., chart speed 40 mm/hr) showed peaks of Fe_2O_3 only. The absence of kamacite, taenite and FeO peaks indicated that oxidation was complete, in spite of the large grain size. (In his investigation into the oxidation techniques discussed above, von Michaelis showed that oxidation proceeded from kamacite via FeO to Fe_2O_3. Incomplete oxidation was evident from the appearence of FeO peaks on the diffractogram.)

For achondrites, a preheating period of 20 hours was considered adequate to oxidize all of the metal present (i.e. acheive constant weight) even in the presence of silicate powder.

The manufacture of the fusion discs was carried out as follows. 0.9 to 1.0 g aliquots of the -200 mesh meteorite powders were weighed into vitreosil crucibles (which had previously been heated to 1000°C for 1 hour), and, after a drying period of about 5 hours at 110°C, were heated at 1000°C. The loss/increase in weight was measured. These powders were then ground in a hand agate pestle and mortar in order to break up the particles of Fe_2O_3 resulting from the oxidation of the metal. In this way, the representative nature of the small sample removed for the manufacture of the fusion discs would be insured. As mentioned previously, the uptake of moisture during this grinding is not likely to result in any serious errors.

0.28 g quantities of powder were removed from this preheated material, mixed with a lithium tetraborate - lithium carbonate - lanthanum oxide flux (Johnson Matthey Spectroflux 105) which had previously been dried at 450°C, and 0.02 g of sodium nitrate added. The mixtures were fused over a Meker burner in an Au-Pt crucible and cast into thin discs as described by Norrish and Hutton (1969). At least three separate discs were made of most samples. For some samples, however, fewer were prepared due to insufficient material being available.

(ii) <u>Pressed briquettes:</u> Trace and some minor elements were determined using undiluted meteorite powders. The -200 mesh powders were mixed with a few drops of distilled water to facilitate binding, placed in a special die, and pressed at 15 tons per square inch to form a small briquette. Backings to these briquettes were made of a bakelite- H_3BO_3 mixture. Details of this procedure have been described by Norrish and Chappel (1967).

SECTION II.

INSTRUMENTAL CONDITIONS.

Introduction.

Two X-ray spectrometers were available for this project - a Philips model PW 1220 Semi-Automatic Spectrometer and an older model PW 1540 instrument. Both instruments were of the flat crystal type. Facilities for pulse height selection were available on both instruments. The PW 1220 was equipped with a 2 kW generator, while the PW 1540 machine had only a 1 kW generator. The composition of the gas in the flow proportional counters of both instruments was 90% argon and 10% methane. Dead times on both detectors was of the order of 3 micro-seconds. Although the equipment was basically standard, certain modifications had been made to the PW 1540 in order to be able to reach higher angles. These involved the filing down on the collimator housing and have been described by Willis et al (1969). On the PW 1220, a choice of two primary collimators was available, viz. 480 micron and 150 micron. The PW 1540 had a single 160 micron collimator permanently fitted. A useful feature available on the model PW 1220 was an exit port on the flow counter, enabling both flow and scintillation counters to be used simultaneously. Both instruments had four sample holders. On the PW 1220, these positions were not equivalent but a difference of up to 2% existed between extremes. This necessitated the use of a position correction on all determinations carried out on this spectrometer.

Major and some minor elements.

Major and some minor elements (Si, Al, Ca, K, Mg, Fe, P, Mn and Ti) in the meteorite samples were determined using the PW 1220 spectrometer. The method of analysis is basically similar to that of Norrish and Hutton (1969). Nevertheless, the approach used here did differ in some respects. A reference sample was counted before and after each set of three samples. This reference sample was a fusion disc which contained fairly high concentrations of all the elements of interest, and hence gave fairly high count rates. All the results for a given element were normalised to a common reference count. In this way, correction for long term instrumental drift was made. Such drift is particularly prevalent in the case of the flow counter, which was the detector used for all these elements. Working curves were established using natural rock standards. These rock standards and their adopted concentrations are presented in Table 1. The intensity measured on the samples was then used to calculate a nominal concentration in the sample from the working curves. This process was repeated for all elements. Nominal concentrations were then used to calculate a matrix coefficient (absorption coefficient) as described by Norrish and Chappel (1967) and Norrish and Hutton (1969). The factors used in the calculation of the matrix coefficients are given in Table 2. Measured intensity was corrected using this coefficient, and concentration again calculated from the working curves. Converged concentrations were obtained on a third such iteration. This computation was done with the aid of an ICL 1301 computer, using programs written by Mr. J. P. Willis.

Instrumental conditions used in these determinations are presented in Table 3. All determinations were carried out under vacuum, and the detector used was the flow proportional counter. Each disc was counted once for the period indicated in Table 3. K_α lines were used throughout.

Some points regarding the selection of instrumental variables deserve special mention. In the determination of Mn, the LiF (220) crystal was preferred to the LiF (200) in spite of the greater reflecting efficiency of the latter crystal (Jenkins and De Vries 1968). LiF (200) has a poorer dispersion than LiF (220). This poses a problem

TABLE 1

Standard Concentrations used in the Analysis of Meteorites for Major and Some Minor Elements.[1]

	BR	GH	T-1	GSP-1	S-1
Fe_2O_3[2]	12.96	1.33	6.03	4.33	8.21
MnO	0.21	0.05	0.11	0.04	0.40
TiO_2	2.62	0.09	0.59	0.69	0.48
CaO	13.74	0.65	5.19	2.03	10.1
K_2O	1.40	4.78	1.23	5.49	2.63
SiO_2	38.20	75.80	62.65	67.28	59.57
Al_2O_3	10.20	12.50	16.52	15.16	9.30
MgO	13.28	0.03	1.89	0.96	4.19
Na_2O	-	-	-	-	-
P_2O_5	1.04	0.01	0.14	0.29	0.22

	W-1	PCC-1	DTS-1	OK272[3]	G-1
Fe_2O_3	11.09	-	-	-	-
MnO	0.17	-	-	-	-
TiO_2	1.07	-	-	-	-
CaO	10.96	-	-	-	-
K_2O	0.64	-	-	-	-
SiO_2	52.64	-	-	-	-
Al_2O_3	14.85	-	-	-	-
MgO	6.62	43.56	49.80	-	-
Na_2O	2.15	-	-	5.29	3.32
P_2O_5	0.14	-	-	-	-

[1] Sources of data: Fleischer M. Geochim. Cosmochim. Acta, <u>33</u>, p65 (1969); Flanagan F.J. ibid., p81; Sine N.M., Taylor W.O., Webber G.R. and Lewis C.L. ibid., p121; Roubault M., de la Roche H. and Govindaraju K. Sci. de la Terre. XIII No. 4 p378(1968); Thomas W.K.L. Tanganyika Geological Survey Suppl. No 1 (1963).

[2] Total Fe expressed as Fe_2O_3

[3] Departmental standard.

TABLE 2

Matrix Correction Factors.

Wave-length	Element											
	Fe	Mn	Ti	Ca	K	P	Si	Al	Mg	Na	Cr	Flux
Fe	-0.027	-0.031	0.146	0.134	0.126	-0.060	-0.065	-0.074	-0.090	-0.110	0.244	1.046
Mn	-0.044	-0.044	0.146	0.135	0.130	-0.063	-0.063	-0.074	-0.078	-0.100	-0.092	1.045
Ti	0.081	0.077	0.179	0.647	0.644	0.181	0.110	0.078	0.069	0.051	0.033	0.851
Ca	0.090	0.092	0.065	0.130	0.723	0.182	0.128	0.105	0.068	0.051	0.036	0.865
K	0.098	0.086	0.017	0.000	0.069	0.179	0.119	0.101	0.080	0.057	0.028	0.897
P	0.108	0.094	-0.020	-0.037	-0.047	-0.063	0.127	0.110	0.094	0.046	0.043	0.896
Si	0.082	0.086	-0.034	-0.042	-0.055	-0.061	-0.061	0.122	0.093	0.063	0.050	1.014
Al	0.112	0.116	-0.032	-0.037	-0.048	-0.060	-0.088	-0.072	0.116	0.058	0.054	1.056
Mg	0.136	0.126	0.010	-0.021	-0.043	-0.016	-0.070	-0.078	-0.084	0.080	0.073	1.050
Cr	0.069	0.060	0.698	0.631	0.647	0.136	0.102	0.084	0.061	0.040	0.028	0.853

TABLE 3

Instrumental Conditions for the Determination of Major and some Minor Elements in Meteorites.

Element	Ti	Ca	K	Si	Al	Mg
Tube	Cr	Cr	Cr	Cr	Cr	Cr
kV	50	50	50	50	50	50
mA	12	12	20	32	32	32
Coll. (μm)	480	150	480	480	480	480
Crystal	LiF(200)	LiF(200)	LiF(200)	PET	PET	ADP
Time(sec)	10	10	20	20	60	240
°2θ	86.88	112.98	136.48	108.94	144.77	136.49

Element	P	Fe	Mn	Bgrnd.	Na
Tube	Cr	W	W	Cr	Cr
kV	50	60	60	50	50
mA	32	32	32	32	32
Coll. (μm)	480	150	150	480	480
Crystal	Ge	LiF(220)	LiF(220)	Gypsum	Gypsum
Time(sec)	120	10	60	60	240
°2θ	140.70	86.48	94.98	96.00	102.95

for meteorite analysis as the Mn K_α and the Cr K_β lines are not resolved by the LiF (200) crystal, resulting in excessive interference from the abundant meteoritic chromium. Therefore, the LiF (220) crystal was preferred. The crystal selection for the determination of Mg and P has been discussed by Norrish and Chappel (1970). Counting times for Mg are relatively long, largely because of low intensities measured. Mg data are therefore particularly prone to error caused by short term instrumental drift.

Sodium was not determined on the fusion discs, but on pressed pellets as suggested by Norrish and Hutton (1970). The background was estimated by taking a measurement near the K_α line. The system of referencing above was also used for the determination of Na. Instrumental conditions for the determination of Na are listed in Table 3. Pulse height selection was used to improve the peak/background ratio. Following Norrish and Hutton (1970), no matrix correction was made for Na, since, for this element, oxygen dominates as the absorber, and this does not vary much from sample to sample.

Minor and Trace Elements.

The remaining minor and trace elements investigated in this work were determined on pressed briquettes. Matrix effects in samples of this form are severe, particularly in view of the range in bulk composition in the samples and standards.

(i) Methods of Matrix Correction.

A variety of methods for correcting matrix effects are available. Two forms of correction were applied in this work. The heaviest major element in most of the samples studied here is Fe. Therefore, for wavelengths shorter than the K absorption edge for Fe (1.744 Å), no abrupt changes in mass-absorption coefficients are likely to occur. Thus, a single measurement of mass absorption where μ_{matrix} is the sample mass absorption coefficient, c_i the weight fraction of component i in the sample and μ_i the mass absorption coefficient of the element under consideration (Jenkins and De Vries, 1968). Values of μ_i given by Birks (1963) were used.

Corrections for primary absorption are complicated by the fact that a range of wavelengths are responsible for the excitation of any particular element. In an attempt to simplify the situation, it was assumed that the bulk of the excitation of any element being determined was induced by the wavelength immediately to the short wavelength side of the relevant absorption edge for that element. The matrix absorption for this wavelength was calculated from the bulk chemistry of the sample using the above equation. The relative contributions of primary (μ_p) and secondary (μ_s) absorption coefficients were weighted according to the geometry of the instrument and combined by means of the the equation

$$\mu_{\text{matrix}} = \mu_p + 1.567\mu_s.$$

Absorption coefficients calculated in this way were used in the determination of Ba, K and Cr.

(ii) Potassium.

Because of the relatively low potassium content of achondrites and HL chondrites, this element was determined using the undiluted briquettes, as well as by the Norrish fusion method.

Analysis using the briquettes was carried out on the PW 1220 spectrometer under vacuum. The potassium K_α line was used for the analysis, with a flow proportional counter to detect the radiation. The instrumental conditions used in the determination are listed in Table 4. A system of reference counting was used to minimise the effect of long term machine drift as discussed above. A single background position was counted, as the background in this region is essentially flat.

TABLE 4.

Instrumental Conditions for the Determination of K in Undiluted Briquettes.

	K K_{α}	Background.
Tube	Cr	Cr
kV	50	50
mA	32	32
collimator (μm)	150	150
crystal	LiF (200)	LiF (200)
time (s)	60	60
$^{o}2\theta$	136.58	143.0

A correction was applied for the absorption of primary radiation. The wavelength used for this correction was 3.360 Å, (Ca K_{α}). Results were calculated with the aid of an IBM 1130 computer. A Fortran IV program was written by the author for this purpose. This program may be found in Appendix I. (The same program was also used for the calculation of the Cr data.)

A single standard was used for the determination of K, viz. W-1. The adopted values of potassium in this standard for these analyses was 5310 ppm. Unfortunately, no suitable standards at lower concentrations were available.

(iii) Chromium.

The determination of Cr by X - ray fluorescence is complicated by interference on the Cr K_{α} line by the V K_{β} line. In meteorite analysis, however, this problem may be ignored, as Cr usually exceeds 0.1% while V is present at about the 100 ppm level (Wiik 1970, Ahrens and Danchin 1971). For similar reasons the effect of a Cr Rayleigh scattered line arising from a slight amount of Cr present in the X - ray tube was ignored. Hence, the method for determining Cr used in this work is similar to that adopted for K, viz. a single background position is measured in addition to the analytical line, and both primary and secondary absorption corrections are made. For this reason, the same computer program used to calculate the K data was used for Cr (See Appendix I.)

Cr was determined on both the PW 1540 and PW 1220 spectrometers. In both cases, the K_{α} line was used and the determinations were carried under vacuum with the flow proportional counter as detector. A reference was used to monitor drift. Instrumental conditions are listed in Table 5. A correction for absorption of primary radiation was made. The wavelength used for this purpose was 1.437 Å, the Zn K_{α} wavelength. Theoretically, the Fe K_{α} wavelength should be used, viz. 6.937 Å, as this is closest to the K absorption edge of Cr (2.070 Å). Empirical studies in this department (H. Fesq pers. comm.) have shown the Zn wavelength to produce superior results. The reason for this probably relates to the presence of the W L_{α} line close to the Zn K_{α} wavelength and this line, together with the white continumuum of even shorter wavelength, is largely responsible for the Cr excitation.

TABLE 5.

Instrumental Conditions for the Determination of Cr in briquettes.

	PW 1220 Spectrometer		PW 1540 Spectrometer.	
	Cr K_{α}	Background	Cr K_{α}	Background
Tube target	W	W	W	W
kV	60	60	50	50
mA	32	32	20	20
Collimator(μm)	150	150	160	160
Crystal	LiF(220)	LiF(220)	LiF(220)	LiF(220)
Time(s)	60	60	120	60
$^{\circ}2\theta$	107.10	99.00	107.05	110.80

Unfortunately, standards present a considerable problem in the determination of Cr. W - 1 was unsuitable due to V interference as well as its low Cr abundance. PCC and DTS are ideal standards for the purpose. Unfortunately, there is little agreement on abundances of Cr in these rocks, as is evident in the values listed by Flanagan (1969). (See Table 6 of this work.)

TABLE 6.

Range of Cr abundance in PCC and DTS-1 by different workers.
(After Flanagan 1969)

PCC-1 (ppm)	DTS-1 (ppm)
1843-4780	2800-5560

In an attempt to resolve this situation, two high Cr BCS standards were diluted ten times with Johnson-Matthey Specpure SiO_2, and fused in a similar way to the method used for major elements. These were then used to standardize similar fusion discs of PCC and DTS. Cr contents

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Data in Table 7 from Willis (pers. comm.) and Bureau of Analysed Samples, Ltd., List No 404, 1962.

	%Cr_2O_3
BCS 308	41.5
BCS 370	14.6

Corrections for absorbtion were made as described by Norrish and Chappel (1967) and Norrish and Hutton (1969). The factors used for this purpose are listed in Table 2.

During the course of this standardization, it became apparent that other factors which tended to complicate the analysis were involved. Firstly, the ratio of corrected counts on DTS and PCC for fusion discs differed by 10% from that on pressed briquettes. This is probably the result of particle size effects. Secondly, the few meteorites examined gave consistently higher values on the pressed briquettes than on fusion discs, even though the same values of PCC and DTS were used in both cases. This effect was probably caused by two factors, one being particle size effects, and the second being enhancement of Cr radiation by the high Fe content of the meteorites concerned.. For those meteorites analysed by both methods, the ratio of the concentration by fusion to concentration by pressed briquette remained constant, indicating that whatever effects were operative causing the discrepancy between standards and samples, it was constant for these samples.

Fe in diogenites, howardites and eucrites was essentially constant at 14% so any enhancement effects are likely to remain constant for all. For this reason, a working curve based on meteorite samples was preferred to that based on PCC and DTS. This was used to calculate the concentrations of Cr in the pressed briquettes. Strictly, this calibration curve is only valid for diogenites, howardites and eucrites, as these have essentially constant Fe, and Cr probably occurs in them in the same form. (See below).

The meteorites used to construct the working curve covered a wide range in composition, as may be seen in Table 8.

TABLE 8.

Cr in Meteorite "Standards". (%)

Shalka	1.66
Frankfort (T)	0.69
Juvinas	0.23

Although results are probably internally consistent, the actual accuracy hinges on the adopted values of the BCS standards. The possibility of some systematic error cannot be ruled out, and, in fact, it was found that such errors are present in the data. (See below).

The standardisation was carried out on the PW 1220 spectrometer. The Cr K_α line was used, in spite of a high background resulting from a La $L_{\beta_{10}}$ line. Various blanks were used to correct for this tailing. Instrumental conditions are listed in Table 9. A reference system was employed, and each disc was counted at least twice. In some cases, duplicate discs were counted as well.

TABLE 9

Instrumental Conditions for Cr Standardisation

Tube	W
kV	60
mA	32
Coll. (μm)	150
Crystal	LiF(220)
Time (s)	100
$^o2\theta$	107.10

(iv) Barium:

This element was determined on the PW 1540 spectrometer, using the method of Willis et al (1969) based on the measurement of the Ba L_α line, with certain modifications as suggested by Kable (pers. comm.). A background position was measured on each sample in preference to the method of blanks as originally suggested by Willis et al (1969). Correction for Ti tailing was made by establishing the ratio of intensity in the Ba L_α position to the intensity of the Ti K_α peak using various SiO_2 - TiO_2 mixtures. Measured counts on the Ti peak for each sample could then be used to ascertain the extent of the tailing on the Ba line. Correction for absorption of primary radiation was made using the wavelength 2.291 Å (Cr K_α). A reference was counted before and after each set of three samples. The flow proportional counter was used to detect the radiation. Instrumental conditions used are listed in Table 10.

TABLE 10

Instrumental Conditions for the Determination of Barium.

	Ba L_α	Bgnd.	Ti K_α
Tube	Cr	Cr	Cr
kV	50	50	50
mA	20	20	20
Coll. (μm)	160	160	160
Crystal	LiF(220)	LiF(220)	LiF(220)
Time (s)	180	180	30
$^\circ 2\theta$	124.31	112.00	119.76

G-1 and W-1 were used as standards. The concentration of Ba in these standards are listed in Table 11.

TABLE 11

Barium in Rock Standards.

W-1	160 ppm
G-1	1040 ppm

Results were calculated with the aid of an IBM 1130 computer using a Fortran IV program written by Mr. E.J.D. Kable.

(v) Strontium:

Strontium was determined by two methods, one on its own, and the other along with Rb, Y and Zr. The former method is described here. The determination was carried out on the PW 1540 spectrometer. The Sr K_α line was used for the analysis. No vacuum was necessary, and no referencing system was used because of the superior stability of the scintillation counter. Instrumental conditions used are listed in Table 12. Simultaneously with the measurement of the Sr peak, the Mo K_α Compton peak was measured, using a fixed time method, as a measure of mass absorption coefficient. Conditions used are listed in Table 13. An average of three readings was taken on each sample.

TABLE 12

Instrumental conditions for the Determination of Sr.

	Bgnd.	Sr Kα	Bgnd.
Tube	Mo	Mo	Mo
kV	50	50	50
mA	20	20	20
Coll.(μm)	160	160	160
Crystal	LiF(220)	LiF(220)	LiF(220)
Time(s)	120	240	120
°2θ	37.00	35.87	35.00

TABLE 13

Instrumental Conditions for the Measurement of the Mo Compton Peak.

Tube	Mo
kV	50
mA	20
Coll.(μm)	160
Crystal	LiF(220)
Counts.	128000
°2θ	30.12

The Mo tube is ideal for the determination of Sr as the Mo K lines are well situated for the exitation of the Sr Kα line. Further, the method is entirely self-contained, as mass absorption coefficient can be estimated in the same run as the Sr line intensity is measured. The LiF(220) crystal was preferred to the LiF(200) in this instance to ensure that background positions were free from tailing by Rb and Y Kα lines, particularly on the standard.

Blank samples, free of Sr and of a range of absorption coefficients were counted to ascertain the relationship between the sum of the two background positions and the Sr peak position. This factor was then used to estimate backgrounds under the Sr peaks of the samples. A factor method such as this was preferred to a linear extrapolation as the background in this region actually follows a curve. A single standard, W-1, was measured simultaneously with the samples. This standard was counted numerous times throughout the run. The Sr content of W-1 was taken as 186 ppm.

A Fortran IV computer program (written by the author) was used in conjunction with an IBM 1130 computer to calculate the results. This program appears in Appendix I.

(vi) Rubidium, Strontium, Yttrium and Zirconium.
These four elements were determined on the same run using a technique similar to that described by Cherry et al (1970) for Rb and Sr. The determinations were carried on both the PW 1540 and the PW 1220 spectrometers. Instrumental conditions used are listed in Table 14.

TABLE 14

Instrumental Conditions for the Determination

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Concentrations of all elements in standard W-1 from M.Fleischer (Geochim. Cosmochim. Acta 33, 65, (1969)) except Sr, where the value recommended by Willis (pers. comm.) has been used.

Coll. (μm)	160	160
Crystal.	LiF(220)	LiF(220)
Time(s)	240	120

Angular positions: ($^{o}2\theta$) Backgrounds. 31.00, 33.00, 35.00, 37.00 and 39.00.
Peaks. Zr - 32.11, Y - 33.90 Sr - 35.87, Rb - 38.00.

PW 1220 spectrometer:

	Peaks	Bgnds.
Tube	W	W
kV	60	60
mA	33	33

TABLE 14 (cont.)

	Peaks	Bgnds.
Coll.(μm)	150	150
Crystal	LiF(220)	LiF(220)
Time(s)	60	60

Angular positions: (°2θ) Backgrounds. 30.80, 33.10,
34.60, 37.00 and 39.00
Peaks. Zr - 32.03, Y - 37.75
Sr - 35.72, Rb - 37.87.

K_{α} lines were used throughout, and a scintillation counter was used to detect the radiation. The analysis for these four elements is complicated by the fact that the Rb K_{β} and Y K_{α} and Sr K_{β} and Zr K_{α} are not resolved by the crystal, necessitating corrections. These were applied by determining the ratio of the intensity of the Rb K_{α} and Sr K_{α} lines tothe intensity of their respective K_{β} lines at the angular positions of Y K_{α} and Zr K_{α} respectively. The measured Rb and Sr K_{α} intensities on the samples could then be used to ascertain the extent of the interference on the Y and Zr K_{α} lines respectively. The ratio between the K_{α} and K_{β} lines is unlikely to change in the suite of samples studied here, as no major absorption edges separate these lines.

Backgrounds under the peaks were determined using a factor method as described in part (iv). Background positions were carefully selected to avoid tailing. These were checked for possible tailing on the powder most enriched in these four elements by plotting the background counts graphically and fitting a line with the aid of a spline curve. The absence of tailing was evidenced by the good fit of the five background points to this line.

These determinations were based on a single standard, viz. W-1. It is ideally suited to the purpose and contains greater abundances of all four elements than any meteorite studied in this work. The concentrations adopted are listed in Table 15. The standard was counted numerous times throughout the run, and an average result was used

TABLE 15

Rb, Sr, Y and Zr content of W-1 (ppm).

Rb	Sr	Y	Zr
21.5	186.0	25.0	100.0

to compute the data. Correction for matrix effects was made using the method of Mo Compton peak measurement described previously.

Results were calculated on an IBM 1130 computer using a Fortran IV program written by the author for the purpose. This program may be found in Appendix I.

(vii) Nickel:

This analysis was carried out on the PW 1220 spectrometer. The analysis for Ni is complicated, firstly by a curved background, and secondly by the presence of trace quantities of Ni in the X-ray tube used, which caused interference on the analytical line by Rayleigh scattering. Due to the possibility of tailing and the fact that the background is curved, four background positions were measured and a curve fitted graphically to the plotted points using a spline curve. The intensity of the background under the Ni K_α line was thus obtained. Correction for interference fron the Rayleigh-scattered line was accomplished by ascertaining the ratio of the Au L_α line to to the peak intensity of the Ni K_α line, using samples free of Ni. The Au L_α line on the samples was measured and this ratio used to ascertain the extent of the tube contribution to the Ni K_α line. As detector sensitivity for both flow and scintillation counters is low in the wavelength region of Ni K_α, both detectors were used simultaneously. Actual instrumental conditions used are presented in Table 16.

TABLE 16

Instrumental Conditions for the Determination of Ni.

	Bgnd.	Ni K_α	Au L_α
Tube	Au	Au	Au
kV	55	55	55
mA	36	36	36
Coll. (μm)	150	150	150
Crystal	LiF(220)	LiF(220)	LiF(220)
Time(s)	100	200	10
°2θ	+	71.18	53.17

+ Background positions: 64.80, 66.40, 69.50 and 73.50.

Results are based on W-1 (78 ppm Ni), which was counted a number of times during the course of the run.

SECTION III

THE ANALYTICAL DATA AND AN ASSESSMENT OF THEIR QUALITY.

Results.

Numerous classifications have been proposed for stony meteorites, and before presenting the data, the classification adopted in this work will be outlined. Carbonaceous chondrites have a relatively well established classification viz. that originally proposed by Wiik (1956). In this work this scheme has been adopted, although the group studied will be referred to as 'HL' as suggested by Keil and Fredriksson (1964), and used by Keil (1969a). In the opinion of the author, Wiik's original nomenclature for carbonaceous chondrites, viz. Types I, II and III should be dropped as this can lead to confusion with van Schmus and Wood's (1967) petrologic types. In contrast, no uniformity exists in achondrite nomenclature, particularly for the so-called Ca-rich or Basaltic achondrites, which form a large part of this study. Traditionally, achondrites have been divided into a Ca-poor and a Ca-rich type (Mason 1960). As will be discussed in a later section, the distinction between these two types is not clearcut. Further, amongst the Ca rich achondrites, two criteria for subdivision have been suggested. Mason (1967) proposed a subdivision based on the relative proportions of ortho-and clino-pyroxene, with ortho-pyroxene dominating over clino-pyroxene in the howardites. The difference in mineralogy between the howardites and eucrites is reflected in their chemistry. Thus, howardites are characterised by lower CaO contents and lower FeO/(FeO+MgO) ratios than eucrites. Duke and Silver (1967), on the other hand, have suggested that the nature of the brecciated structure be used as the criterion for subdividing howardites and eucrites. In their system, howardites are recognized as being polymict breccias, while eucrites are regarded as monomict. In terms of this classification, Binda, a meteorite which has a bulk composition similar to some howardites is classified as a eucrite. Inthis work, the classification of Duke and Silver (1967) has been adopted, as it is considered to be genetically more meaningful than the system of Mason. This is discussed at greater length in a later section.

There seems to be no standard form for presenting meteorite analyses. Some authors, e.g. von Michaelis el al (1969), present meteorite analyses in the form of elements, while others prefer to list data as oxides, sulphides, etc. (for example, Jarosewich 1966). As the analyses presented in this work are in some ways incomplete, the data will be presented in element form. The analytical data are presented in Table 17.

The data for major and minor elements represent averages of at least two and in most cases more replicate analyses of the same meteorite powder. Before averages were calculated, the data were carefully screened for errors, and any analysis obviously in error was excluded. An individual analysis was excluded if the total differed by more than 2% from the average of replicate determinations, or if any individual component differed by more than 3% relative from the mean of that component. In applying these criteria, it was found necessary to exclude only one analysis, where insufficient sample resulted in an erroneous result.

The trace element data represents, in most instances, averages of replicate determinations. These data have also been carefully screened. Where replicate trace analyses for a meteorite differed by more than the combined uncertainty due to counting statistics (at the 3σ level), the meteorite was reanalysed. If this failed to resolve the problem, an average of the analyses was calculated.

Quality of the data.

Although H.S.Washington, as early as 1917, had emphasised the question of the quality of silicate analyses, this issue was brought home to meteoritics by Urey and Craig in 1953, who managed to classify only 94 analyses out of

TABLE 17

Analytical Data

	Serra de Mage	Stannern	Bereba	Juvinas	Pasamonte
Fe %	12.58	13.82	14.83	14.63	14.93
Mn %	0.426	0.406	0.426	0.433	0.438
Ti %	0.100	0.587	0.422	0.383	0.434
Ca %	6.49	7.62	7.49	7.42	7.36
Cr %	0.37	0.23	0.22	0.23	0.21
P %	0.025	0.045	0.046	0.040	0.047
Si %	22.64	23.24	22.97	23.07	22.57
Al %	6.71	6.53	6.75	6.88	6.52
Mg %	6.85	4.21	4.10	4.38	3.96
Na %	nd	0.46	0.34	0.46	0.38
K ppm	60	549	294	340	356
Sr ppm	nd	91	78	77	77
Zr ppm	nd	98	53	48	57
Y ppm	nd	33	23	20	24
Ba ppm	nd	50	33	31	33
Ni ppm	nd	<dl	<dl	<dl	5

\+ denotes find
<dl below detection limit
nd not determined

TABLE 17 (cont.)

	Sioux County	Haraiya	Cachari$^+$	Macibini	Binda $^+$
Fe %	14.44	14.97	14.85	14.23	13.08
Mn %	0.432	0.459	0.459	0.418	0.418
Ti %	0.370	0.335	0.379	0.430	0.139
Ca %	7.41	7.33	7.33	7.12	3.99
Cr %	0.24	0.22	0.22	0.29	0.51
P %	0.030	0.042	0.036	0.048	0.018
Si %	22.92	22.76	22.56	23.06	23.51
Al %	6.80	6.61	6.80	6.41	3.69
Mg %	4.29	4.29	4.31	5.05	10.71
Na %	0.33	0.37	0.38	0.36	0.15
K ppm	295	270	411	399	85
Sr ppm	74	71	83	74	32
Zr ppm	42	37	41	59	18
Y ppm	22	19	19	25	6
Ba ppm	28	25	48	36	11
Ni ppm	13	<dl	<dl	23	6

	Malvern	Chaves	Zmenj	Frankfort (T)	Frankfort (F)
Fe %	14.02	11.92	13.39	13.91	13.50
Mn %	0.411	0.371	0.405	0.434	0.427
Ti %	0.293	0.219	0.192	0.136	0.170
Ca %	5.76	4.03	3.89	2.60	3.28
Cr %	0.38	0.42	0.55	0.76	0.69
P %	0.039	0.025	0.020	0.015	0.020
Si %	22.98	24.21	23.40	23.79	23.78
Al %	5.27	3.62	3.43	2.26	2.88
Mg %	7.48	11.09	10.41	12.63	11.63
Na %	0.31	0.16	nd	0.16	0.15
K ppm	379	176	160	108	128
Sr ppm	57	38	nd	22	28
Zr ppm	35	31	nd	15	20
Y ppm	16	10	nd	6	7
Ba ppm	22	17	nd	8	11
Ni ppm	274	34	nd	48	63

TABLE 17 (cont.)

	Johnstown	Ellemeet	Tatahouine	Shalka	Chassigny
Fe %	12.64	13.48	11.77	12.65	21.34
Mn %	0.387	0.439	0.384	0.428	0.413
Ti %	0.072	0.034	0.041	0.037	0.040
Ca %	1.04	0.57	0.54	0.52	0.42
Cr %	0.59	1.29	0.50	1.65	0.57
P %	0.006	0.003	0.003	<dl	0.018
Si %	25.07	24.08	25.58	24.11	17.30
Al %	0.65	0.49	0.27	0.32	0.19
Mg %	15.62	16.29	17.03	15.55	19.80
Na %	0.02	0.08	0.02	0.03	0.11
K ppm	20	27	<dl	13	268
Sr ppm	<dl	<dl	<dl	<dl	5
Zr ppm	<dl	<dl	<dl	<dl	<dl
Y ppm	<dl	<dl	<dl	<dl	<dl
Ba ppm	<dl	<dl	<dl	<dl	4
Ni ppm	90	21	15	5	494

	Cumberland Falls(ach)	Norton County	Shallowater^{+}	Cumberland Falls(ch)
Fe %	2.11	1.26	12.14	14.70
Mn %	0.140	0.191	0.042	0.298
Ti %	0.027	0.034	0.013	0.068
Ca %	0.77	0.93	0.28	1.43
Cr %	0.074	0.070	0.066	0.46
P %	0.008	<dl	0.106	0.066
Si %	26.12	25.21	21.43	20.69
Al %	0.21	0.12	0.50	1.03
Mg %	22.65	25.16	18.89	17.33
Na %	0.17	0.07	0.36	nd
K ppm	190	55	425	869
Sr ppm	<dl	<dl	6	nd
Zr ppm	<dl	<dl	<dl	nd
Y ppm	<dl	<dl	<dl	nd
Ba ppm	21	<dl	15	nd
Ni ppm	371	314	7600	nd

TABLE 17 (cont.)

	Vigarano	Mokoia	Allende	Leoville^{+}
Fe %	22.24	22.59	23.55	22.02
Mn %	0.147	0.155	0.157	0.146
Ti %	0.104	0.091	0.091	0.091
Ca %	2.26	2.00	1.84	1.80
Cr %	0.40	0.42	0.43	0.40
P %	0.093	0.097	0.101	0.095
Si %	15.25	15.30	16.00	15.55
Al %	2.07	1.82	1.74	1.83
Mg %	14.41	14.32	15.10	14.86
Na %	0.28	0.36	0.36	0.11
K ppm	319	306	300	100
Sr ppm	16	15	14	13
Zr ppm	11	7	8	8
Ba ppm	4	5	4	4

	Coolidge^{+}	Lancé	Warrenton	Felix
Fe %	24.00	24.65	25.43	25.30
Mn %	0.125	0.169	0.175	0.172
Ti %	0.087	0.074	0.075	0.075
Ca %	1.66	1.53	1.57	1.54
Cr %	0.44	0.44	0.45	0.46
P %	0.103	0.103	0.107	0.106
Si %	15.64	15.55	16.01	16.05
Al %	1.67	1.35	1.40	1.38
Mg %	14.92	14.27	15.10	14.85
Na %	0.20	0.35	0.43	0.36
K ppm	129	397	390	371
Sr ppm	14	12	13	12
Zr ppm	8	7	9	6
Ba ppm	11	3	8	4

286 as superior, even though the criteria they used would not today be regarded as very exacting. Mason (1965) has reinvestigated the question of quality of data, and formulated certain criteria for assessing quality. In addition, numerous other workers have made observations on the quality of the available data (see von Michaelis 1969). More recently, the question of the quality of data has been brought into sharp focus by the work of von Michaelis et al (1969b). Their work showed that much of modern data were of insufficient quality to show inter-relationships of various elements in chondrites. In this regard, Figure 1 of Ahrens and von Michaelis (1969a) is very pertinent.

The quality of meteorite data is dependant not only on the analysis itself, but also on the nature of the sample. Obviously, non-representative sampling can destroy the usefulness of an analysis, although this is not always the case. In this work, an attempt was made to obtain as large samples as possible, which, it was hoped, would be free of the problem of non-representative sampling (see page 6). The analytical technique used in this work has been shown to be capable of producing data of good quality, and it was hoped that by analysing representative aliquots of relatively large crushed samples, data of a fairly high quality would be obtained for a relatively large number of achondrites. The purpose of this section is to assess this data, with a view to establishing whether this aim has been achieved.

Various schemes have been suggested for assessing the quality of major element analyses of meteorites. Urey and Craig (1953) initiated these. Mason (1965) proposed a more rigorous approach. He based his assessment on:

a) Accuracy, gauged by the degree of correlation between the FeO/(FeO+MgO) ratio calculated from the analysis and that measured in the ferro-magnesian minerals,

b) Summation, represented by the closeness of the total of the major components in the analysis to 100%,

c) The completeness of the analysis.

Unfortunately, such a scheme is not applicable here. In the case of the HL chondrites studied in this work, only total iron is known, so the FeO/(FeO+MgO) ratio is likely to be in error. Further, Ni has not been determined so that both the criteria of summation and completeness cannot be satisfied completely. In the case of the achondrites, the reliability of available optically determined FeO/(FeO+MgO) ratios are questionable, particularly in view of the age of many of these determinations (some date back prior to 1920). Keil and Fredriksson (1964) have also suggested that errors up to 10% may occur in optically determined FeO/(FeO+MgO) ratios in ferromagnesian minerals.

Other criteria have also been used to assess the quality of major element data. Of particular interest is the use by von Michaelis et al (1969) of the spread of inter-element ratios and element abundance in various types of meteorites. In addition to this criterion, these authors used a direct comparison of their data with that in the literature, probably the most widely used method of establishing the quality of data.

In this work, a procedure similar to that used by von Michaelis el al will be used. The reproducibility for the fusion technique of analysis was ascertained by taking thirteen separate aliquots of a homogeneous rock powder through the entire sample preparation (crushing excepted) and analytical procedures. The possibility of systematic error was investigated by direct comparison of the data obtained in this study with that in the literature. Finally, where possible, various rock samples of known composition were analysed simultaneously with the samples. This served as a further check on accuracy.

Major and some Minor elements.

Results obtained by the fusion method are discussed in terms of their accuracy and the precision of the technique used.

a) Precision: A homogeneous dolerite powder was split into thirteen portions, and taken through the entire analytical procedure in order to determine analytical precision. Further, individual discs were distributed randomly amongst the sample discs, and not counted consecutively. The precision thus obtained, which includes every step of the technique, thus accurately reflects that for the samples. Statistical data calculated from these thirteen analyses are presented in Table 18.

TABLE 18

Analytical Precision for Fusion Determinations.

	Average of 13 analyses	Standard Deviation	Coefficient of Variation
Fe_2O_3	11.059	0.074	0.671
MnO_2	0.176	0.002	1.688
TiO_2	0.879	0.007	0.904
CaO	10.968	0.064	0.586
K_2O	0.659	0.003	0.458
P_2O_5	0.194	0.008	4.166
SiO_2	51.272	0.409	0.798
Al_2O_3	15.985	0.131	0.819
MgO	6.551	0.101	1.541
Na_2O	2.250	0.024	1.070
H_2O^-	0.119	0.019	16.353
H_2O^+	0.210	0.047	22.679

(Total Fe is expressed as Fe_2O_3)

Careful examination of Table 18 is instructive. For most elements, the precision, as expressed by the coefficient of variation, is good ($<1\%$). Some rather interesting features may be noted. For example, the precision for Mg is considerably poorer than that for K, although the former is about 10 times more abundant. The reason for this is the relatively long wavelength of Mg, and hence the long counting times required, which makes this element particularly prone to short-term instrumental drift. The precision for P is particularly poor, probably resulting from a combination of low abundance and relatively long wavelength. This seems to be substantiated by comparing this data with Mn, which is present in a similar abundance but has a superior precision. The poor precision as far as H_2O^+ and H_2O^- are concerned is probably partly due to the imprecision in the weighing of small changes in weight, although some variation must be real. The reasons for this are not clear.

b) Accuracy: As mentioned above, the accuracy of meteorite analyses can be ascertained by comparison with the data in the literature. The most satisfactory method of comparison is obviously to compare average compositions of fairly large numbers of analyses of members of groups which are uniform in composition. Of the meteorites studied in this work, eucrites and HL chondrites are best suited to such a comparison, as a reasonably large number have been analysed. Howardites are of more variable composition with respect to most elements, and will not be used in all comparisons. Where possible, the data of this work are compared to those published by specific workers individually, and in most cases only post-1960 analyses have been used. It is assumed that inferences regarding the quality of data based on HL chondrites and eucrites applies equally to the other achondrite types studied. Broadly speaking, the abundance levels in eucrites and HL chondrites encompass those found in classes not considered in the comparisons. In calculating group averages of eucrites, Binda and Serra de Mage have been ommitted, as these are unusual eucrites (this work and Schnetzler and Philpotts 1968).

(i) Iron: Ahrens and von Michaelis (1969b) and Ahrens and Danchin (1971) have stressed the limited spread of Fe in eucrites and howardites, despite the marked variation in other major components such as Ca, Al and Mg. The range in iron abundance in eucrites and howardites analysed in this work is comparable with that found by other workers as may be seen in Figure 11 and Table 19.

TABLE 19

Comparison of Fe abundances obtained in this work with those obtained by other workers.[+]

Analyst	Method	Eucrites	
		Range	Mean
von Michaelis et al (1969b)	XRF	14.35-14.37	14.36(2)
Schmitt et al (1971)	NAA	11.6 -18.5	14.8 (15)
Duke and Silver (1967)	-	14.35-15.75	14.89(5)
Nichiporuk el al (1967)	XRF	12.93-14.52	13.75(6)
This work	XRF	13.82-14.97	14.58(8)
		Howardites	
		Range	Mean
Wiik (1970)	'Classical'	13.20-13.96	13.64(4)
Schmitt et al (1971)	NAA	11.0 -19.1	13.6 (9)
This work	XRF	11.92-14.02	13.30(5)
		HL	
		Range	Mean
von Michaelis et al (1969b)	XRF	22.33-24.60	23.10(4)
Wiik (1970)	'Classical'	24.04-26.18	25.17(9)
Schmitt et al (1971)	NAA	20.0 -28.6	24.1 (9)
This work	XRF	22.24-25.43	23.63(8)

[+] Data expressed as weight % Fe.

The extreme variation in the Fe content of meteorites analysed by Schmitt et al (1971) probably reflects non-representative sampling. (Sample sizes used by these authors ranged from 0.014 to 1.24g.) This is suggested by the poor agreement with the data of other analysts for individual meteorites. For example, Schmitt et al found Sioux County to contain 17.1% Fe as compared with 14.35% by Duke and Silver (1967), 12.39% by Nichiporuk et al (1967), 14.35% by von Michaelis et al (1969b) and 14.44% in this work.

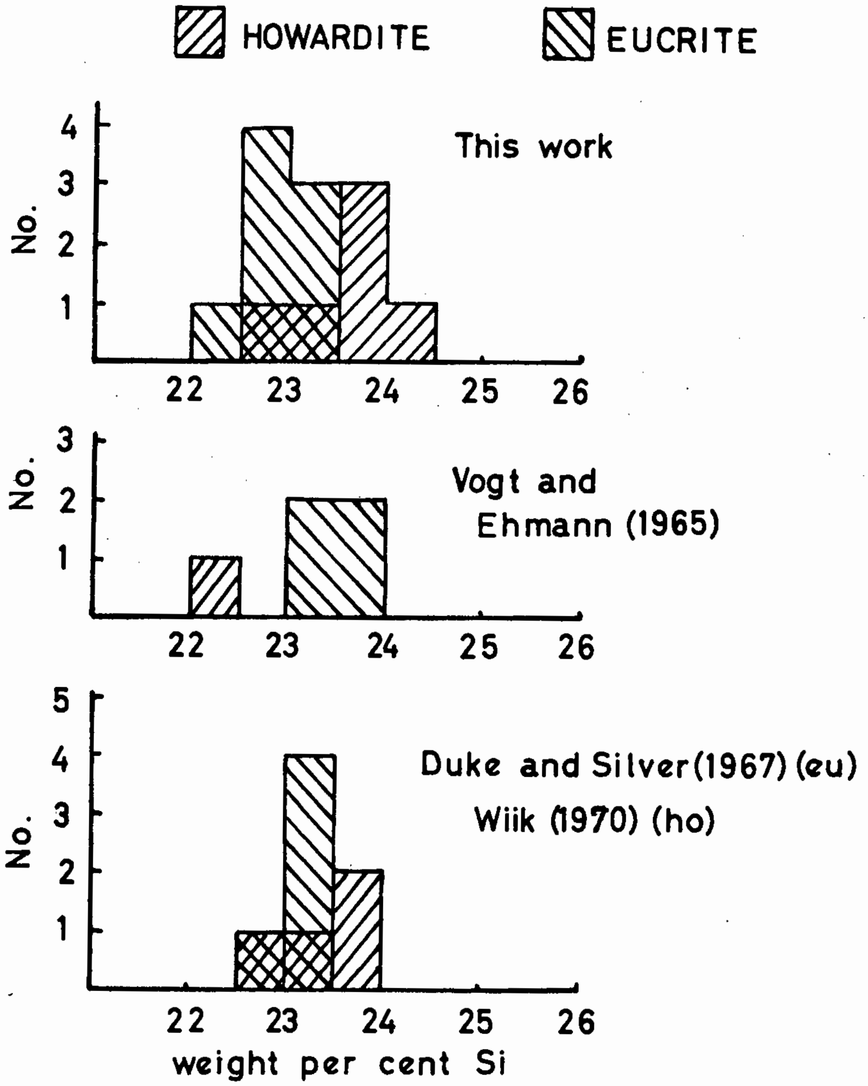
The limited spread of the data obtained in this work for Fe attests to their high quality, not only from the analytical aspect, but also from the point of view of the representative nature of the samples. Further, group averages obtained in this work compare favourably with those obtained by other workers, indicating the probable absence of large systematic errors. Although the standard with the highest Fe content contained less Fe than the HL chondrites, the calibration curve is nevertheless linear over the entire range of iron concentration encountered in this work. This has also been confirmed by Willis (pers. comm.) who analysed artifically prepared Fe_2O_3/SiO_2 mixtures using the same technique.

It appears from the analyses presented here that iron is slightly fractionated between eucrites and howardites. This fact is not apparent in the body of data collected by Ahrens and Danchin (1971), but may be seen in the combined data of Duke and Silver (1967) and Wiik (1970), if one accepted the absence of systematic error. The analyses presented here confirm this absence. It will become apparent in a later section that this fractionation of Fe is not discrete, but is related to the composition range exhibited by the howardites.

(ii) Silicon: The silicon abundance in howardites and eucrites, like that of iron, is remarkably uniform. This has been pointed out by Ahrens and by Ahrens and Danchin (1971). In fact, the latter authors go so far as to state that '...the dispersion of SiO_2 in the basaltic achondrites ($c = 1.1\%$) is about the same as that of the analytical data on homogenised powder of one rock, standard W-1.'

The analytical data for howardites and eucrites obtained in this work is compared to some recent data by other workers in Figure 2. Analytical data in general for Si compares favourably with that obtained by other workers. A slight fractionation of Si between howardites and eucrites is apparent from the data presented here. As will be shown in a later section, this fractionation is related

figure 2



Frequency distribution diagrams of Si in howardites and eucrites for the data of various analysts.

to the composition variation exhibited by the howardites. Further comparison of data may be found in Table 20.

TABLE 20

Comparison of Si abundances (wt. %) obtained in this work with those obtained by other workers.

Analyst	Method	Eucrites Range	 Mean
Duke and Silver (1967)		22.71-23.21	23.01(5)
Vogt and Ehmann (1965)	NAA	23.3 -23.6	23.5 (4)
von Michaelis et al (1969b)	XRF	22.38-22.94	22.66(2)
This work	XRF	22.44-23.24	22.88(8)
		Howardites Range	 Mean
Wiik (1970)	'Classical'	22.63-23.56	23.21(4)
This work	XRF	22.98-24.21	23.61(5)
		HL Range	 Mean
Vogt and Ehmann (1965)	NAA	15.3 -16.1	15.7 (4)
von Michaelis et al (1969b)	XRF	15.55-16.29	15.84(4)
Wiik(1970)	'Classical'	14.32-15.24	15.50(9)
This work	XRF	15.24-16.05	15.61(8)

Average Si concentrations obtained here agree favourably with those obtained by other workers using a variety of methods, indicating the absence of systematic errors.

(iii) Manganese: Like Si and Fe, this element has also been shown to remain at a constant abundance level in both howardites and eucrites by Ahrens and Danchin (1971). No fractionation of Mn between eucrites and howardites was observed in the data of this work. This data is compared to that of other workers in Table 21.

TABLE 21

Comparison of Mn abundances (wt. %) obtained in this work with those obtained by other workers.

Analyst	Method	Eucrites	
		Range	Mean
Schmitt et al (1971)	NAA	0.15 - 0.58	0.38(15)
Duke and Silver (1967)	-	0.39 - 0.43	0.41(5)
von Michaelis et al (1969b)	XRF	0.415-0.421	0.418(2)
Nichiporuk et al (1967)	XRF	0.37 -0.47	0.40(5)
This work	XRF	0.41 -0.46	0.43(8)
		Howardites	
		Range	Mean
Schmitt et al (1971)	NAA	0.37 - 0.43	0.39(9)
Wiik(1970)	'Classical'	0.40 - 0.43	0.41(4)
This work	XRF	0.37 - 0.44	0.42(6)
		HL	
		Range	Mean
Schmitt et al (1971)	NAA	0.13 - 0.17	0.15(10)
Wiik(1970)	'Classical'	0.15 - 0.18	0.16(9)
von Michaelis et al (1969b)	XRF	0.129- 0.165	0.150(4)
This work	XRF	0.12 - 0.18	0.16(8)

Average abundances obtained in this work compare favourably with those of other workers. The range in the data of Schmitt et al (1971), particularly for eucrites, is again evident, probably due to poor sampling.

(iv) Magnesium: Only data for eucrites and HL chondrites are compared to literature data, as howardites are known to exhibit a range in Mg abundance (e.g. Mason 1967, Duke and Silver 1967). Average Mg abundances of other workers are compared to those obtained here in Table 22. No gross systematic error is evident in the Mg data presented in this work.

TABLE 22

Comparison of Mg data obtained in this work with that obtained by other workers+

Analyst	Method	Eucrites	HL
Duke and Silver (1967)	-	3.94(5)	-
Wiik (1970)	'Classical'	-	14.42(9)
von Michaelis et al (1970)	XRF	-	14.59(4)
This work	XRF	4.32(8)	14.55(8)

+ Data expressed as wt. % Mg

(v) Calcium and Aluminium: The importance of the abundance relationship between Ca and Al in stony meteorites has been stressed by Ahrens and von Michaelis (1969a,b) and Ahrens (1970c), and these elements are therefore discussed together. Average Ca and Al abundances in eucrites and HL chondrites obtained by various workers are compared to those obtained in this work in Tables 23 and 24 respectively.

TABLE 23.

Comparison of Ca Data.+

Analyst	Method	Eucrites	HL
Nichiporuk et al (1967)	XRF	7.23(6)	-
Duke and Silver (1967)	Classical	7.43(4)	-
Wiik (1970)	Classical	-	1.59(9)
von Michaelis et al (1969b)	XRF	-	1.84(4)
This work	XRF	7.38(8)	1.77(8)

+ Data expressed as wt. % Ca.

TABLE 24

Comparison of Al Data+

Analyst	Method	Eucrites	HL
Loveland et al (1969)	NAA	6.38(6)	1.37(8)
Duke and Silver (1967)	'Classical'	6.59(5)	-
von Michaelis et al (1969)	XRF	-	1.70(4)
Wiik (1970)	'Classical'	-	1.46(9)
This work	XRF	6.66(8)	1.65(8)

+ Data expressed as wt. % Al

Average Ca and Al abundances of the data obtained in this work agree reasonably well with those of other workers, indicating the absence of large systematic errors in the data reported here.

Ahrens and von Michaelis (1969a,b) and Ahrens (1970c) have shown that the Ca/Al ratio in chondrites, howardites and eucrites remains essentially constant over a wide range of Ca and Al abundance levels. The average Ca/Al ratio obtained by these authors was 1.08. This ratio not only provides a critical check on the quality of data, but, in addition, in the case of the howardites and eucrites it also provides a test, albeit somewhat insensitive, on the representative nature of the samples, as the relative proportions of plagioclase and clino-pyroxene must be fairly well balanced in order to produce a Ca/Al ratio of 1.08. (The theoretical maximium Ca/Al ratio in plagioclase is 0.74). The relative contributions of non-representative sampling and inferior quality analytical data on the Ca/Al ratio are obviously difficult to distinguish in a small number of analyses.

Ca/Al ratios obtained in this study are compared to some recent determinations by other workers in Table 25.

TABLE 25

Comparison of Ca/Al ratios.

	Eucrites	
	Range	Mean
Literature[1]	1.09-1.16	1.12
This work	1.08-1.17	1.11(8)
	Howardites	
	Range	Mean
Literature[2]	1.02-1.15	1.06
This work	1.08-1.15	1.12(5)
	HL	
	Range	Mean
Literature[3]	0.91-1.37	1.11
This work	0.98-1.13	1.07(8)

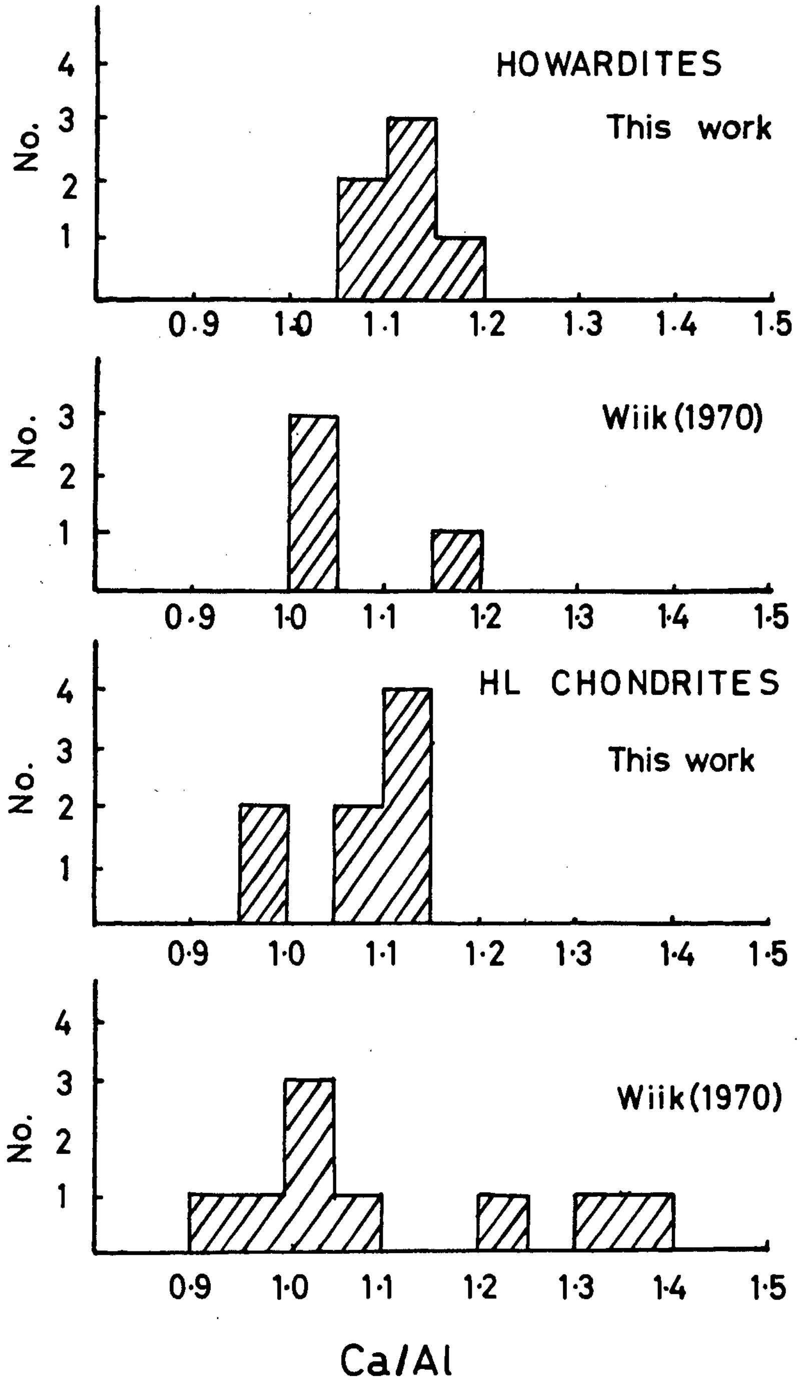
1. Average of four eucrites. Data from Duke and Silver (1967), Engelhard(1963) and von Michaelis et al (1969b).
2. Average of five howardites. Data from Wiik (1970) and von Michaelis et al (1969b)
3. Average of nine chondrites. Data from Wiik (1970) and von Michaelis et al (1969b)

The data of this work compare favourably with recent analyses of high quality. Further comparison of data is shown in Figure 3, where howardites and HL chondrites analysed in this work are compared histogramatically with analyses of a single analyst of some repute, viz. H. B. Wiik.

The spread of Ca/Al ratios in HL chondrites obtained by Wiik is considerably greater than that found in this work, indicating the superiority of XRF data at low levels of Ca and Al. In the howardites, this is not quite as marked indicating that wet chemical methods used by Wiik produce data of comparable quality to XRF at relatively high Ca and Al abundance levels. The data presented in this work suggest a slight fractionation of the Ca/Al ratio in HL chondrites. At least two groups are clearly recognizable on this basis. A third group may exist as well. These sub-groups, with their corresponding Ca/Al ratios are shown in Table 26. Ca/Al ratios for both Wiik (1970) and von Michaelis et al (1969) data have been included in this table as well.

The level of significance of the Ca/Al ratios for the data presented here have been estimated using the analytical precision for Ca and Al presented in Table 18. At the 2σ level, Ca/Al ratios are significant to within ±0.022 for Lancé and ±0.015 for Vigarano, the HL chondrites with the lowest and highest Ca respectively. Leoville and Coolidge have significantly lower Ca/Al ratios than the remaining six HL chondrites. Within this latter group there is a suggestion of a fractionation of the Ca/Al ratio, although this does not stand up to rigorous statistical tests.

figure 3



Frequency distribution diagrams of the Ca/Al ratio in howardites and HL chondrites for the data of this work and of H.B.Wiik.

TABLE 26

Possible sub-groupings amongst the HL chondrites based on Ca/Al ratio fractionation.

Meteorite	Type$^+$	This work	von Michaelis et al (1969b)	Wiik(1970)
		Ca/Al	Ca/Al	Ca/Al
Leoville	C4-V(?)	0.98	-	0.91
Coolidge	C4-V	0.99	-	-
Vigarano	C3-V	1.09	1.05	1.05
Mokoia	C2-V	1.10	1.09	1.37
Allende	C3-V (?)	1.06	-	-
Lancé	C3-O	1.13	1.12	1.21
Warrenton	C3-O	1.12	-	1.34
Felix	C3-O	1.12	1.07	1.01

\+ C2, C3 and C4 denote the petrologic groups of van Schmus and Wood (1967). V and O refer to the Vigarano and Ornans sub-types of the HL chondrites respectively (van Schmus 1968). Classification from Clarke et al (1971)

(vi) Titanium: Ti data obtained in this work are compared to that of other workers in Table 27. Howardites exhibit a range in Ti abundance and have therefore been excluded.

TABLE 27

Author	Method	Eucrites$^+$	HL$^+$
Duke and Silver (1967)	-	0.46(5)	-
Wiik (1970)	'Classical'	-	0.09 (9)
von Michaelis et al (1969b)	XRF	-	0.087(4)
This work	XRF	0.417(8)	0.086(8)

\+ Data expressed as wt. % Ti

Average abundances of Ti in eucrites and HL chondrites obtained in this work are in good agreement with those of other analysts.

(vii) Sodium: Sodium analyses carried out by X-ray fluorescence are not regarded as being of a particularly high standard. In this work, no absorption correction was applied for this element. Further, counting times are long, making the results susceptible to instrumental drift. These difficulties are reflected in the measured precision for the Na determination. The data obtained in this work are compared to literature values in Table 28. No serious systematic errors are evident in the Na reported in this work.

TABLE 28

Comparison of Na data+

Analyst	Method	Eucrites	HL
Schmitt et al (1971)	NAA	0.32(14)	0.34(9)
Duke and Silver (1967)	-	0.36(5)	-
Wiik (1970)	'Classical'	-	0.42(8)
Tera et al (1970)	AA	0.3451(6)	-
This work	XRF	0.39 (8)	0.30 (8)

+ Data expressed as wt. % Na

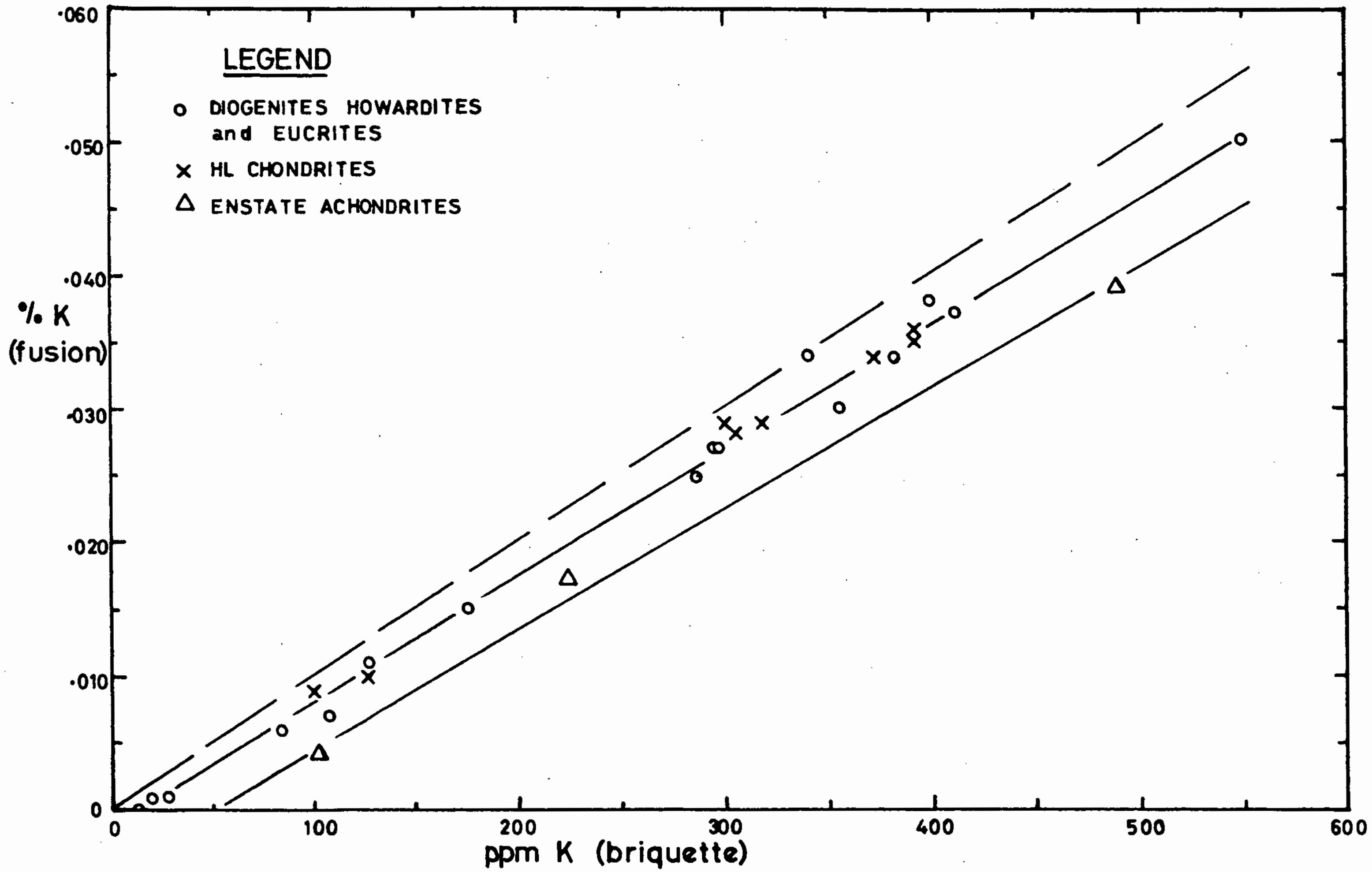
(vii) Potassium: As discussed in Section II, potassium has been determined by two methods on most of the samples, viz. on the fusion discs and on pressed powder briquettes. A comparison of the data obtained by the two methods is instructive, since, in some cases, insufficient material was available for the preparation of briquettes, and, as K is low in the meteorite studied here, the validity of the fusion determination must be established before the data can be used.

Figure 4 shows a plot of K determined by the fusion method against that measured on the briquettes. A distinct and systematic departure from the 45° line is evident, with the briquette determination being systematically high relative to the fusion data. The data used to construct Figure 4 may be found in Appendix II. The fitted line does not pass through the origin, but intersects the ordinate (briquette determination) at about 15 ppm indicating insufficient background correction on the briquette data

ERRATA

Equation for calculating weighted average of primary and secondary mass absorption coefficients from H.Fesq (pers. comm.).

figure 4



Comparison of K as obtained by two independant methods.
(The dashed line represents the "45° line".)

or over correction on the fusion data. The latter is probably the cause of the error, as the standards and blanks used in this run had already been in use for some ten months prior to this work being carried out. Some K contamination is highly likely in these circumstances. In addition to this error, results obtained by the briquette method are some 9% higher than those obtained by the fusion technique. The reason is not clear. However, a sample of gabbro which has been standardised in this laboratory by a variety of methods (Erlank et al 1968) at 0.169% K was analysed simultaneously with the samples by the briquettes method. A result of 0.170% K was obtained indicating that the extrapolation from W-1 is essentially correct, and that the systematic error occurs in the fusion disc technique. A final check was provided by the sample of Serra de Mage, which was found by the fusion technique to contain 0.004% K. (The detection limit by the fusion technique is 10ppm.) Philpotts and Schnetzler (1970a) have analysed this same powder using isotope dilution techniques, and found it to contain 61 ppm K, a result which is in satisfactory agreement with the fusion value which has been corrected for the systematic errors discussed above.

In addition to the above systematic errors, the K data for the enstatite achondrites seems to be particularly unrelaible. This is most probably due to matrix effects in the briquettes. For this reason, corrected fusion K values are preferred for these meteorites.

Uncertainties in the matrix corrections for the briquettes are probably also responsible for the slight scatter of the points in general.

Because of the range of K abundance in the meteorite types studied in this work, comparisons with literature values are best undertaken using individual meteorites, rather than group averages. These comparisons are shown in Table 29.

TABLE 29

Comparison of K data obtained in this work with that obtained by other analysts

Meteorite	Author	Method	K(ppm)
Juvinas	Tera et al (1970)	ID	322
	Philpotts and Schnetzler (1970a)	ID	298
	This work	XRF	340
Pasamonte	Tera et al (1970)	ID	327
	This work	XRF	356
Stannern	Tera et al (1970)	ID	657
	Philpotts and Schnetzler (1970a)	ID	686
	This work	XRF	549
Bereba	Tera et al (1970)	ID	258
	This work	XRF	294
Sioux County	Tera et al (1970)	ID	305
	This work	XRF	295

Data obtained in this work compares favourably with recent determinations by isotope dilution analysis, and are considered satisfactory for the present purposes.

(ix) Phosphorus: Data for phosphorus obtained in this work are compared to some literature values in Table 30.

TABLE 30

Comparison of P data obtained in this work with that obtained by other analysts^{+}

Author	Method	Eucrites	
		Range	Mean
Duke and Silver (1967)		0.04-0.06	0.05(5)
This work	XRF	0.03-0.05	0.04(8)
		Howardites	
		Range	Mean
Wiik (1970)	'Classical'	0.025-0.05	0.04(3)
This work	XRF	0.02-0.04	0.02(5)

TABLE 30 (cont.)

Author	Method	HL Range	 Mean
Wiik (1970)	'Classical'	0.04-0.17	0.12(9)
This work	XRF	0.09-0.11	0.10(8)

+ Data expressed as wt. % P.

Comparison with the data of other workers is favourable, indicating the absence of gross systematic errors in the data of this work.

Minor and Trace Elements.

a) Precision: The manufacture of briquettes for trace element determination is very reproducible. The factor which is largely responsible for determining the precision of a trace element analysis is therefore the random nature of X-radiation. The statistics related to this distribution are well known, so that analytical precision can readily be calculated. Thus, for example, Willis et al (1969) showed that the precision obtained by counting the Ba Lα line on 11 briquettes of the same sample (c = 2.3%) was very similar to the precision calculated from the measured count rate on one of these briquettes (c = 2.2%). In this work, the precision for each trace element analysis has been calculated using the formulae givenby Norrish and Chappell (1967) (eqns. 32 and 33).

b) Detection Limits: Many of the trace elements studied in this work are present in achondrites in extremely low abundances. An estimation of the detection limits is therefore essential. These have been calculated from background measurements at a level of significance of 3σ using the formula given by Norrish and Chappell (1967) (eqn. 37).

c) Accuracy: The accuracy of trace element determinations by X-ray fluoresence is heavily dependant on the accuracy with which the mass absorption coefficient can be determined. As discussed previously, the Compton peak method of Reynolds (1963) has been used in most instances.

Norrish and Hutton (1969) have pointed out that a 2 g briquette is infinitely thick for all wavelengths at least as short as the Sr Kα line. Most of the samples included in this study exceed this 2 g limit. However, two of the meteorites studied were probably not infinitely thick for the Sr $K\alpha$ wavelength, partly because of their low Fe content (and hence low mass absorption coefficient) coupled with the fact that insufficient material was available. These are Cumberland Falls (achondrite) and Chassigny. This does not present a problem, however, as both these meteorites had contents of Rb, Sr, Y and Zr below the detection limit of the method used.

As in the case of major elements, the quality of the trace element data is assessed by comparison with analyses taken from the literature. In view of the general paucity of data, analyses of individual meteorites have been compared rather than group averages.

(i) Strontium: As mentioned above, Sr has been determined by two, and in some instances three separate techniques, i.e. different instruments and instrumental conditions were used. Results by the different techniques compare favourably and in most cases agree to within the calculated precision. Detection limits and precision (2σ) for the various techniques are listed in Table 31.

TABLE 31

Detection Limits and Precision for the Determination of Sr.

	PW 1540 Mo tube	PW 1540 W tube	PW 1220 W tube
Detection Limit (ppm)	1.5	2.0	2.0
Counting error (ppm)	±1.1	±1.5	±1.5

Sr data obtained in this work are compared to some recent determinations by other workers in Table 32.

As may be seen, the Sr data reported in this work compare very favourably with recent analyses carried out using

TABLE 32

Comparison of Sr data obtained in this work with that obtained by other analysts.

Meteorite	Author	Method	Sr(ppm)
Stannern	Schnetzler and Philpotts (1970)	ID	87.0
	Eberhardt and Geiss (1966)	ID	85.0
	Tera et al (1970)	ID	87.7
	This work	XRF	90
Pasamonte	von Michaelis et al (1969b)	XRF	77
	Gast (1962)	ID	82.7
	Gopalan and Wetherill (1968)	ID	77.8
	Tera et al (1970)	ID	78.0,75.0
	This work	XRF	77
Sioux County	von Michaelis et al (1969b)	XRF	73
	Burnett and Wasserburg (1967)	ID	73
	Gast (1962)	ID	68.8
	Tera et al (1970)	ID	76.0
	This work	XRF	74
Juvinas	Tera et al (1970)	ID	77.1
	This work	XRF	77
Bereba	Tera et al (1970)	ID	74.7
	This work	XRF	78
Malvern	von Michaelis et al (1969b)	XRF	58
	This work	XRF	57
Mokoia	Rama Murthy and Compston (1965)	ID	16.3
	von Michaelis et al (1969b)	XRF	15
	Kaushali and Wetherill (1970)	XRF ID	14.20
	This work	XRF	15
Lancé	Rama Murthy and Compston (1965)	ID	14.7
	von Michaelis et al (1969b)	XRF	12
	This work	XRF	12
Allende	Kaushall and Wetherill (1970)	ID	14.42
	This work	XRF	14

isotope dilution analysis. Rock standards PCC and DTS were included in the determination as cross-checks on the background correction factor, as both have Sr contents below the detection limit of the method used (Flanagan 1969). Results obtained for these rocks indicated the essential correctness of the background factor correction method.

(ii) Barium: The detection limit of the analytical technique employed for the analysis of Ba in this work (Willis et al 1969) is dependant on the concentration of Ti in the sample, as Ti Kα interferes slightly with the Ba Lα line. Approximate detection limits are listed together with estimated analytical precision in Table 33.

TABLE 33

Detection Limits and Precision for the Determination of Ba.

	HL and Ca-poor achondrites	Ca-rich achondrites
Detection Limit (ppm)	1.7	2.6
Counting error (ppm)	±1.2	±2.2

The data obtained in this work are compared to some recent literature values in Table 34.

The data obtained in this study compare favourably with that of other workers. Few HL chondrites have been analysed for Ba, and there does not appear to be much agreement between those which are available. For example, Moore and Brown (1963) find the average Ba content of HL chondrites to be 4.0 ppm, while Greenland and Lovering (1965) obtained a value of 13.4 ppm. An average of 8 ppm was found in this work.

(iii) Zirconium: The detection limit and counting error for Zr are presented in Table 35. Zr data obtained in this work are compared with some recent determinations by other workers in Table 36. It is evident from this comparison that no systematic errors are present in the Zr data presented in this work.

TABLE 34

Comparison of Ba data obtained in this work with that obtained by other analysts.

Meteorite	Author	Method	Ba(ppm)
Stannern	Schnetzler et al (1968) Gast et al (1970) Tera et al (1970) This work	ID ID ID XRF	58 49.2 53.0 50
Sioux County	Gast (1965) Tera et al (1970) This work	ID ID XRF	25 27.2 28
Pasamonte	Gast (1965) Tera et al (1970) This work	ID ID XRF	38 28.6 33
Juvinas	Schnetzler and Philpotts (1968) Tera et al (1970) This work	ID ID XRF	33 30.2 31
Bereba	Tera et al (1970) This work	ID XRF	28.6 33

TABLE 35

Detection Limit and Precision for the Determination of Zr.

Detection limit (ppm)	2.5
Counting error (ppm)	±1.7

TABLE 36

Comparison of Zr data obtained in this work with that obtained by other analysts.

Meteorite	Author	Method	Zr(ppm)
Juvinas	Schmitt et al (1964a) This work	NAA XRF	53 48
Pasamonte	von Michaelis et al (1969b) Ehmann and Rebagay (1970) This work	XRF NAA XRF	58 58,64 57
Sioux County	von Michaelis et al (1969b) This work	XRF XRF	48 42

TABLE 36 (cont.)

Meteorite	Author	Method	Zr(ppm)
Stannern	Schmitt et al (1964a) This work	NAA XRF	70 90
Binda	Ehmann and Rebagay (1970) This work	NAA XRF	17 18

(iv) Yttrium: Detection limits and counting errors for Y are presented in Table 37. Few achondrites and HL chondrites have been analysed for Y. The analyses by Schmitt et al (1964b) for Juvinas (17.1 ppm) and Stannern (28 ppm) agree reasonably well with the values for these meteorites obtained in this work (20 and 33 ppm respectively).

TABLE 37

Detection Limit and Counting Error for the Determination of Yttrium

Detection Limit (ppm)	2.4
Counting error (ppm)	±1.3

(v) Nickel: Unlike its abundance in chondrites, Ni is present in trace amounts in achondrites (Nichiporuk et al 1967). For this reason, Ni was determined on undiluted powders. The success of this technique hinges on the fineness of the metal phase, as Ni occurs largely in this phase. In this form, severe matrix effects could occur in the determination of Ni. The reason is that the Ni K_α analysis line (1.659Å) occurs immediately to the short wavelength side of the Fe K absorption edge (1.744Å) and will therefore be strongly absorbed by the Fe component of the metal phase. If the grain size of the metal is coarse, most of the attenuation of the Ni K_α radiation will be caused by absorption within the metal phase. Calculated absorption coefficients or Compton peak measurements will not correct for this absorption, as these methods give an average absorption coefficient for the entire sample. The results will therefore be in error. If, on the other hand, the metal phase is sufficiently fine so that absorption by the silicate matrix exceeds that occuring in the metal phase, then the applied matrix correction will be satisfactory. Unfortunately, it is not possible to estimate to what extent the data presented here have been affected by such particle size effects since metal particle size distributions are unknown. Nor have oxidized achondrite powders prepared by von Michaelis et al (1969a), which were available for study in this work, been able to throw light on this problem, as sample inhomogeneity with respect to Ni in these samples was too great. For example, two separate oxidized samples of Malvern contained 327 ppm and 221 ppm Ni respectively, while two Johnstown samples contained 137 and 45 ppm respectively.

Two points emerge from this discussion. Firstly, there is every likelyhood that Ni data presented in this work are subject to a variable systematic error, and secondly, that samples are not representative as far as the metal phase is concerned.

The data for Ni obtained in this work do not compare very favourably with the data of other analysts. Some thin-film X-ray fluoresence determinations by Nichiporuk et al (1967) are compared to the data of this work in Table 38.

TABLE 38

Comparison of Ni data obtained in this work with that of Nichiporuk et al (1967).+

Meteorite	This work	Nichiporuk et al (1967)
Binda	6	13
Juvinas	<dl	9
Pasamonte	5	9
Sioux County	8	18
Stannern	<dl	9
Haraiya	<dl	15

+ Data in ppm

(vii) Chromium: Cr data for howardites and eucrites obtained in this study are compared to some recent analyses by other workers in Table 39. The range of Cr in many instances is considerable, probably due largely to sampling problems. The achondrite data in Table 39 suggests the presence of a slight systematic error in the data of this work.

TABLE 39

Comparison of Cr data obtained in this work with that of other analysts.

Meteorite	Analyst	Method	Cr(ppm)
Bereba	Schmitt et al (1971)	NAA	1870
	This work	XRF	2200
Sioux County	Schmitt et al (1971)	NAA	2000,2300 2260
	Nichiporuk et al (1967)	XRF	1420
	Duke and Silver (1967)	-	2460
	This work	XRF	2300
Stannern	Schmitt et al (1971)	NAA	1780
	Nichiporuk et al (1967)	XRF	1250
	Duke and Silver (1967)	-	1920
	This work	XRF	2300
Macibini	Schmitt et al (1971)	NAA	2380,2730
	This work	XRF	2900
Binda	Schmitt et al (1971)	NAA	4070,4350
	Nichiporuk et al (1967)	XRF	6500
	This work	XRF	5100
Frankfort	Schmitt et al (1971)	NAA	5160,4740
	Wiik (1970)		9200
	This work	XRF	7700,7000
Shallowater	Nichiporuk et al (1967)	XRF	517
	This work	XRF	655
Norton County	Nichiporuk et al (1967)	XRF	392
	Schmitt et al (1971)	NAA	570
	This work	XRF	700
Cumberland Falls	Nichiporuk et al (1967)	XRF	427
	Schmitt et al (1971)	NAA	180,730
	This work	XRF	741
Shalka	Nichiporuk et al (1967)	XRF	1.07%
	This work	XRF	1.66%
Johnstown	Nichiporuk et al (1967)	XRF	5300
	This work	XRF	6000

In the case of the HL chondrites, a systematic error is again evident, and is considerably larger than that observed in the achondrite data, as may be seen in the data listed in Table 40. The cause of this is not apparent, but may be due to enhancement by Fe, as well as other matrix effects.

TABLE 40

Comparison of Cr data for HL chondrites +

Meteorite	This work	Wiik (1970)	Nichiporuk et al (1967)	Schmitt et al (1971)
Felix	0.46	0.30	0.35	0.366
Lancé	0.44	0.33	-	0.351, 0.363
Leoville	0.40	0.34	0.34	-
Mokoia	0.42	0.35	-	0.348,0.350,0.336
Vigarano	0.40	0.35	0.34	0.353

+Data expressed as % Cr.

(vii) Rubidium: Data for this element are not reported here, as Rb is present either on or below the detection limit of the method used in all types of meteorites studied in this work.

SECTION IV.

DISCUSSION.

Introduction.

In the past, numerous papers have been published concerning the chemistry of achondrites. These investigations have in many cases, been hampered by poor data, by the complex systems of nomenclature which have existed, and simply by a lack of knowledge of other complimentary aspects of these meteorites. Thus, in earlier studies, all achondrite types have sometimes been grouped together, obviously producing a somewhat complex, and misleading picture (e.g. Cassidy 1958). As our knowledge of meteorites increased, it has become apparent that the absence of chondrules does not necessarily imply a similar genesis for these meteorites. Thus, recent studies of achondrites have tended to be of a more specific nature. A similar approach will be adopted here, particularly where obvious group dissimilarities exist.

DIOGENITES, HOWARDITES and EUCRITES.

1. Inter-element relationships amongst the diogenites, howardites and eucrites.

Unlike other specific meteorite groups (e.g. eucrites, chondrites etc.), the howardites exhibit a large range in composition, in which certain distinct inter-element relationships have been known for some time, and have been discussed by workers in relation to the origin of these meteorites. Furthermore, the association of eucrites and diogenites with the howardites has also been discussed by some workers.

Although most achondrites are brecciated (Mason 1962, Keil 1969a), it became apparent to students of these meteorites that they had been molten at some stage of their history, and most theories for their origin have revolved around this observation. The classic study of the unbrecciated eucrite Moore County by Hess and Henderson (1949) proved beyond doubt that this melting ~~point~~ must have been extensive, as they were able to show that this particular meteorite had been formed by crystal settling in a silicate melt.

Trends in composition amongst the achondrites have been studied by many workers in their efforts to unravel the origin of the achondrites. Cassidy (1958), starting with the assumption that tektites, achondrites and chondrites were genetically related, concluded that processes of liquid immiscibility, or crystal fractionation in a very acid melt, were responsible for the observed composition variations in achondrites. Ringwood (1961), although not elaborating on detailed inter-element relationships, suggested that achondrites might have arisen by melting of a chondrite, with separation of metal and ferromagnesian minerals (pallasites, diogenites and aubrites), leaving a eucritic type material. This suggestion has been further documented and expanded by subsequent studies. Moore (1962), in his examination of achondrite chemistry, showed that the relationship between aubrites on the one hand, and diogenites, howardites and eucrites on the other, was not one of simple igneous differentiation. In contrast, he observed that the variation in bulk composition among the latter groups was regular, and could quite conceivably have been produced by processes of igneous differentiation as suggested by Ringwood. Mason (1962) extended Moore's and Ringwood's suggestion, and related the sequence of pallasites, howardites and eucrites to the phase system SiO_2 - Mg_2SiO_4 - $CaAl_2Si_2O_8$ of Andersen (1915). Mason (1967) has further elaborated this idea, and has shown that a regular increase in CaO with increasing FeO/(FeO + MgO) ratio occurs in the sequence pallasite - diogenite - howardite - eucrite.

More recently, Ahrens and von Michaelis (1969b) have examined the chemical inter-relationships amongst in particular, howardites and eucrites, and have made some observations very pertinent to the origin of these meteorite types. Using modern analyses only, these workers showed that the Ca/Al ratio in chondrites was essentially constant (Ahrens and von Michaelis 1969a) and that this ratio remained unchanged in howardites and eucrites at 1.08, in spite of the increase in absolute abundance of Ca from 0.85% in enstatite chondrites to about 7.4% in eucrites. Howardites themselves are shown to cover a considerable range in Ca (and Al) increasing from 2.77% in Frankfort, to nearly 7%. Eucrites, on the other hand are rather uniform in composition. These authors have also pointed out that Mg decreases regularly with increase in Ca and Al, forming a regular inverse relationship. In spite of these variations, Ahrens and von Michaelis, and Ahrens and Danchin (1971) have observed that over the entire range of Ca, Al and Mg variation, from eucrites on the one extreme to Frankfort on the other, the contents of Fe, Mn and Si remain essentially constant at approximately 14.1%, 48.7% and 0.40% respectively. Further observations by Ahrens (1970a) and Willis et al (1971) have shown positive linear correlation to exist between the element pairs Mg and Cr, Ba and Nd, and Sr and Eu, once again with howardites defining the bulk of the concentration range in each case. As far as these trace element pairs are concerned, eucrites tend to exhibit a spread in concentration, reaching maxima in Nuevo Laredo and Stannern (Ahrens 1970b), as opposed to the major elements (i.e. Ca, Al, Mg) which are somewhat invariant from one eucrite to another.

Some of the inter-element relationships observed by the above-mentioned workers have been investigated in this study with a view to elucidating the origin of the diogenites, howardites and eucrites. In most instances, only the data obtained in this work have been used in order to minimize any systematic inter-laboratory differences, as well as the effects of sample inhomogeneity. The chondrite data of von Michaelis et al (1969b) are considered to be comparable to the data of this work (large samples were analysed by the same technique as used here) and are therefore used for comparative purposes. However, the data of other analysts, where used, have been treated as separate sets.

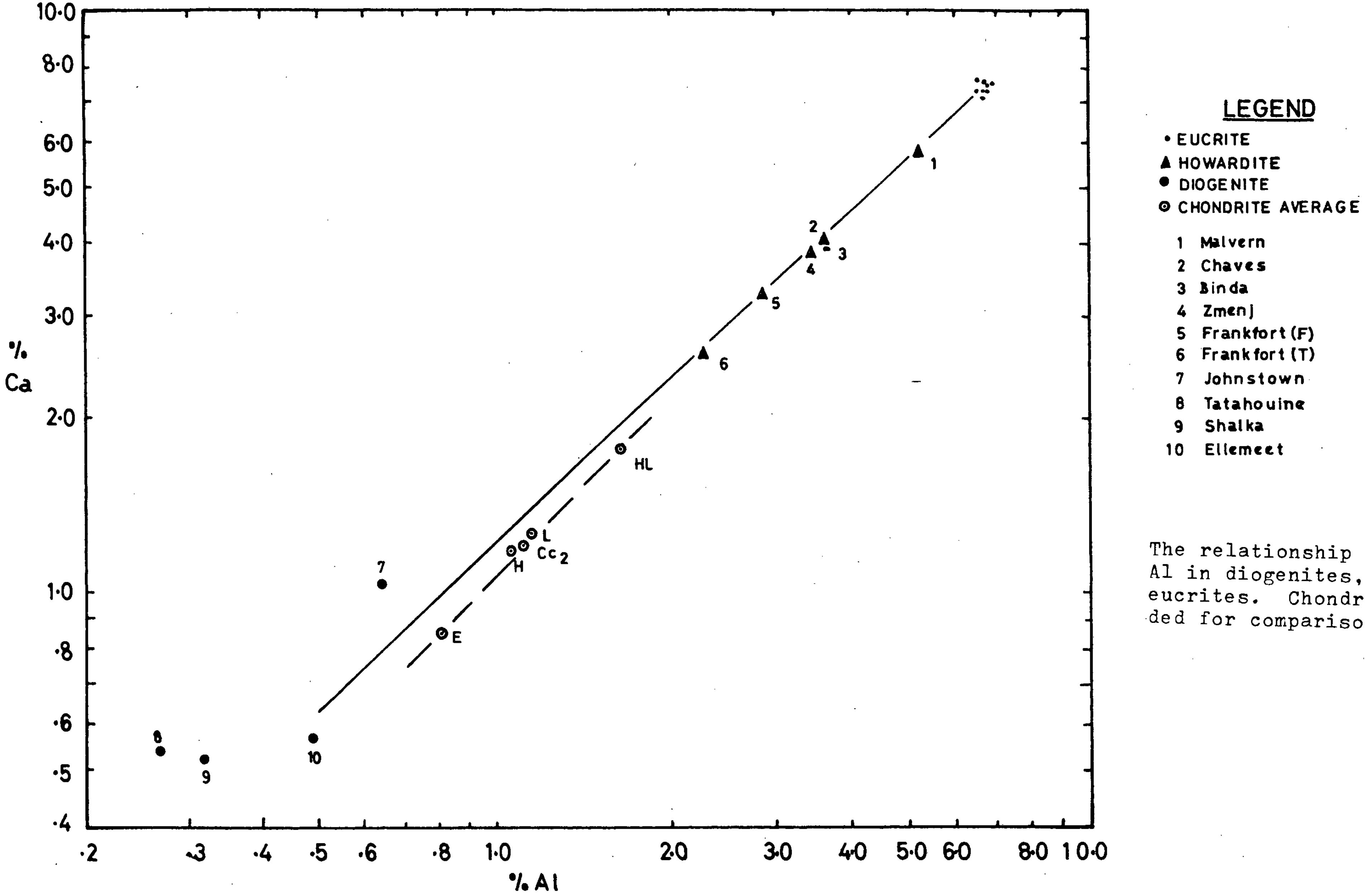
(a) Some relationships between refractory elements.

Ahrens (1970c) has defined the refractory group of elements as comprising Ca, Al, Sc, Ti, Sr, Y, Zr, Nb, Ba, REE, Hf, Ta, Th and U. He has pointed out that all these elements increase in abundance through the howardites to reach maximium meteoritic abundance in the eucrites.

(i) The Ca-Al relationship: The Ca and Al data of this work for diogenites, howardites and eucrites are shown plotted against one another in Figure 5. Included in this figure are the E, H and L group averages of von Michaelis et al (1969b) and the HL average obtained in this work. The Ca/Al ratios of pertinent meteorite groups are shown in Table 41.

Evident both in Figure 5 and Table 41 is a slight tendency for the Ca/Al ratio of howardites to diverge from that of chondrites with decreasing Ca and Al. Unfortunately, no howardites are known to have lower Ca than Frankfort , so this divergance is difficult to confirm. It will be noted that data for two Frankfort samples have been quoted and that these differ significantly in their Ca and Al content. Both meteorites nevertheless lie on the Ca/Al trend line in Figure 5 - in effect, the two samples of Frankfort analysed in this work apparently behave as different, but normal howardites and have therefore, been treated as such. The significance of this observation will be discussed at length in a later section. As may be seen in Figure 5, the Ca/Al ratio of diogenites is variable, but nevertheless significantly greater than that for chondritic

figure 5



The relationship between Ca and Al in diogenites, howardites and eucrites. Chondrites are included for comparison.

exhibit a range in Ti from 0.335% in Haraiya to 0.587% in Stannern. The resultant trend in the Ca-Ti plot contrasts sharply with the broad trend of increasing Ti with Ca as defined by the howardites.

TABLE 41.

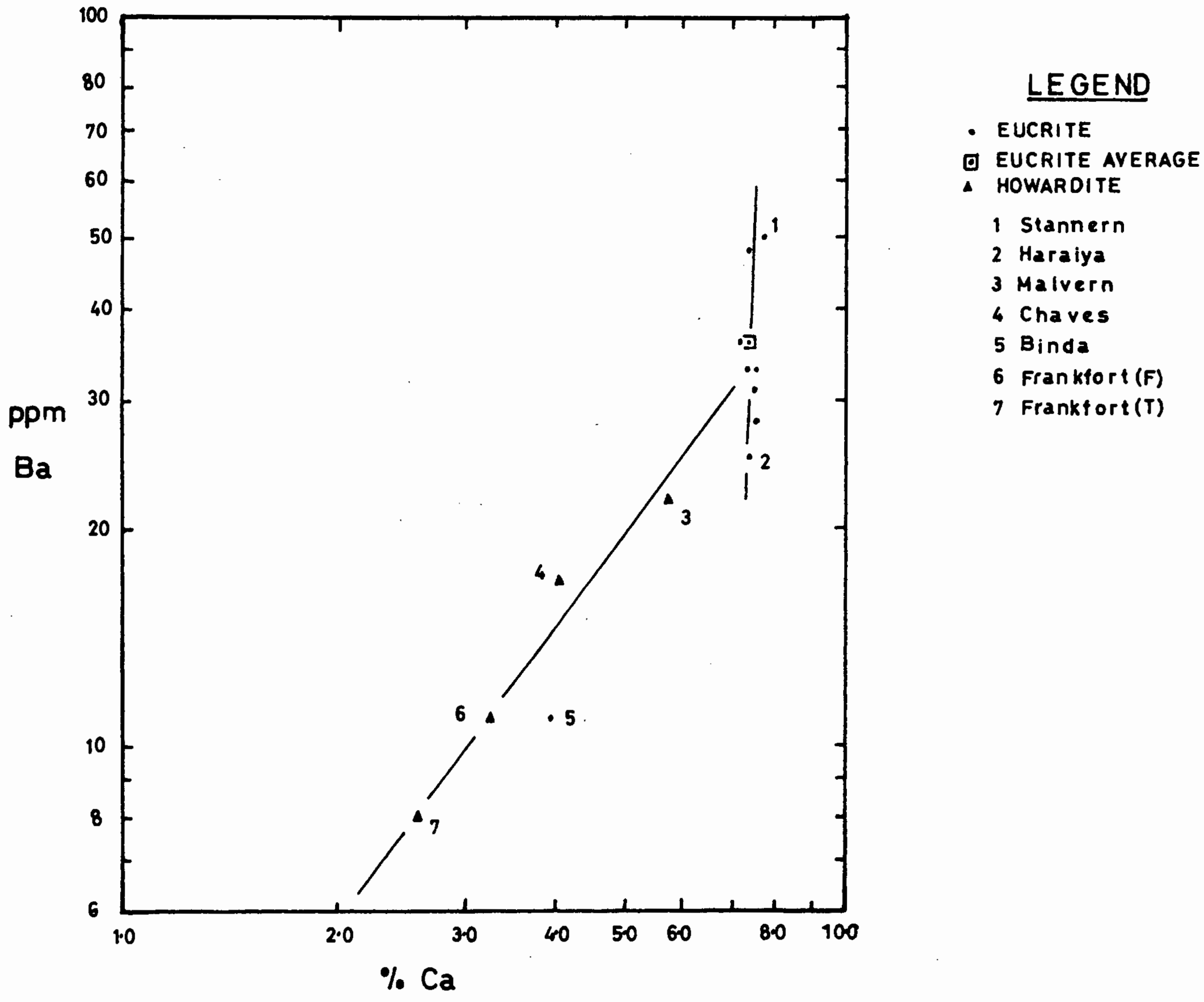
The Ca-Al relationship in chondrites, diogenites, eucrites and howardites.

Meteorite	%Ca	%Al	Ca/Al
Eucrite average (8)	7.38	6.66	1.11
Malvern	5.76	5.27	1.09
Chaves	4.03	3.62	1.11
Binda	3.99	3.69	1.08
Zmenj	3.89	3.43	1.13
Frankfort (F)	3.28	2.88	1.14
Frankfort (T)	2.60	2.26	1.15
Diogenite average (4)	0.67	0.43	1.56
HL average (8)	1.77	1.65	1.07
H average	1.17	1.06	1.10
L average	1.29	1.17	1.10
Enstatite	0.85	0.81	1.05

(iii) The Ca-Ba relationship: This relationship is depicted diagramatically in Figure 7. It exhibits certain similarities with the Ca-Ti relationship discussed previously, in that Binda is depleted in Ba (or enriched in Ca) relative to howardites in general, and that eucrites are observed to exhibit a range in Ba, while Ca is essentially invariant.

A particularly interesting feature of both the Ca-Ba and the Ca-Ti relationships is that the line of best fit to the howardites does not appear to pass through the low Ba and Ti ends of the eucrite trends. Thus, it appears that Haraiya, the eucrite most depleted in the refractory trace elements, does not'follow on' from the howardite trend as might be expected if these trends represented genetic sequences. The actual intersection point of the two trends is difficult to estimate due to the spread in the howardite data.

figure 7



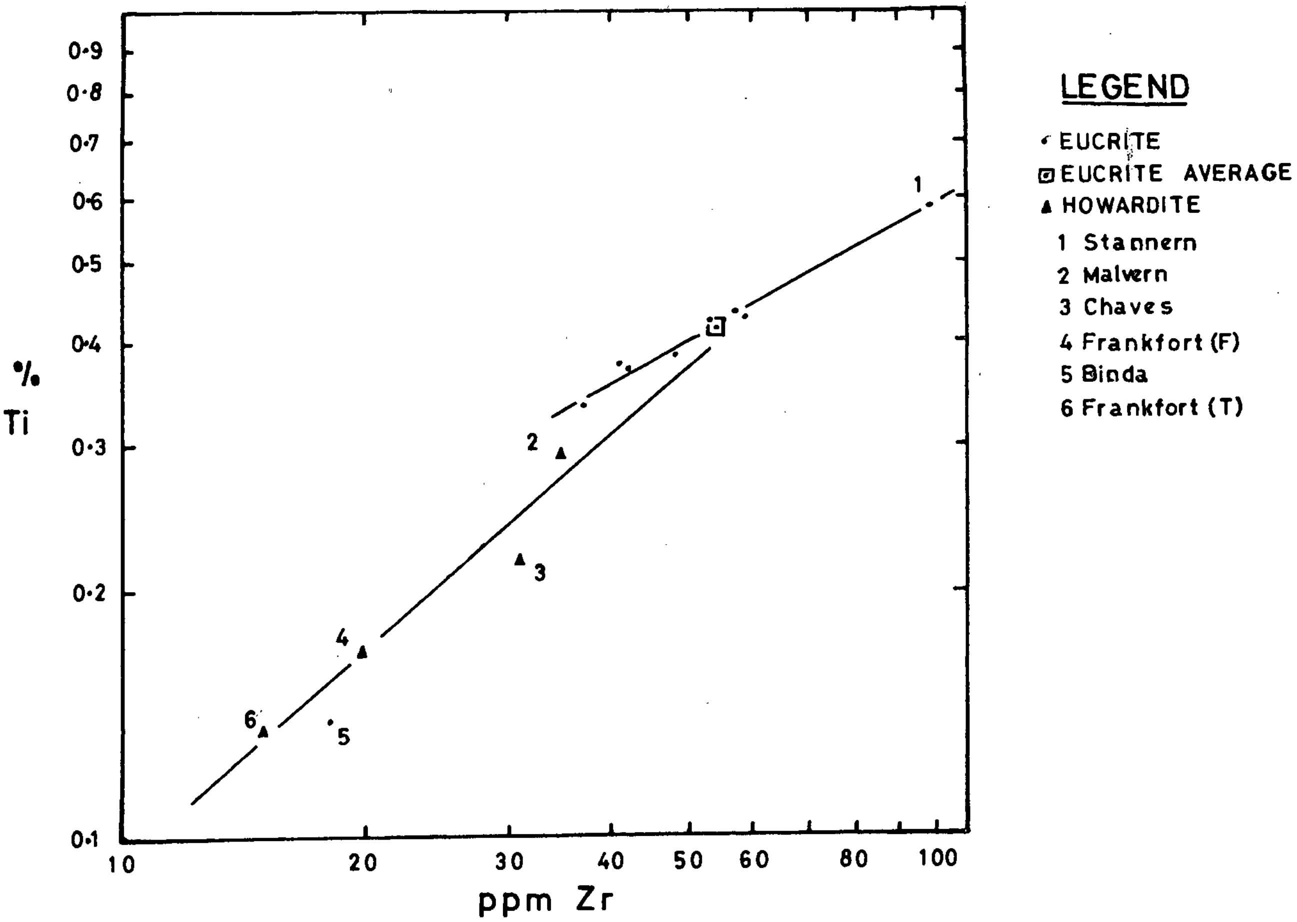
The relationship between Ba and Ca in howardites and eucrites.

(iv) The Zr-Ti and Sr-Ba relationships: Figures 8 and 9 show the relationship between Zr and Ti and Sr and Ba respectively in howardites and eucrites. These diagrams serve to illustrate some of the points mentioned above. The distinctly different trace element trends in howardites and eucrites is immediately obvious. In general, howardites exhibit a greater variability in these trace elements than do the eucrites - i.e. the spread of data is greater for the former meteorites, making the estimation of the intersection point of the two trends almost impossible to pinpoint. The coherence of the eucrite data indicates that this spread in the case of the howardites is real, and not due to analytical error. In the case of the element pairs considered in Figures 8 and 9, the line of best fit through the howardites appears to pass through the average eucrite composition. The depletion of Binda in Zr and Ti relative to howardites is evident in Figure 8, where the relative positions of Frankfort (F) and Binda observed in the Ca/Al plot (Figure 5) have actually been reversed.

In both Figures 8 and 9, but, particularly in the former, a distinct hiatus exists between Stannern and the remaining eucrites. In Figure 9, this gap is partly filled by the anomalous eucrite Cachari, in which both Ba and Sr are enriched relative to Ti, Zr (and Y). This hiatus is probably the result of non-representative sampling of the eucrite population. It will be recalled that Stannern is not alone in showing enrichment in refractory trace elements. Nuevo Laredo is known to exhibit similar features (Ahrens 1970b).

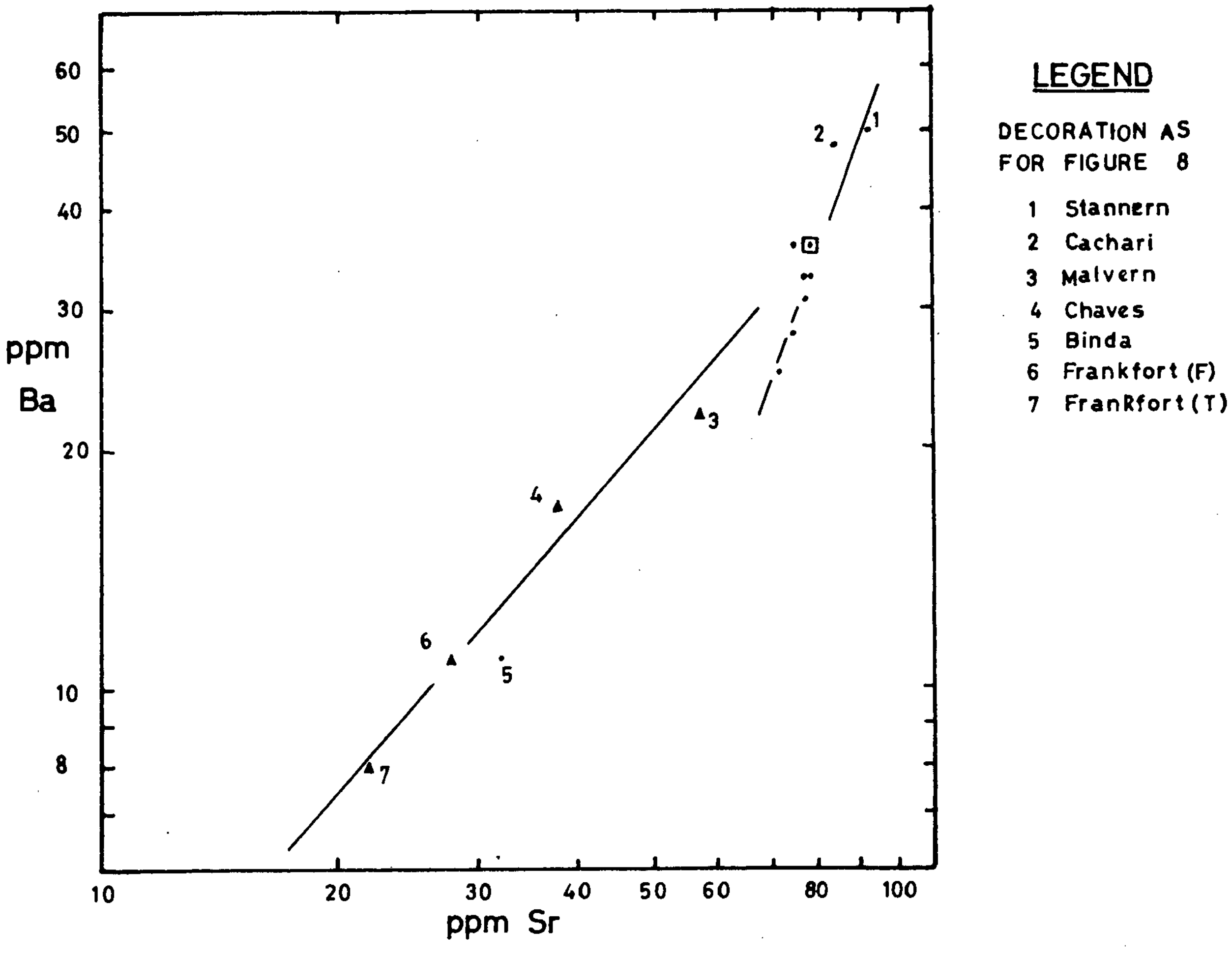
The relationships between the refractory elements discussed here are by no means unique. Similar observations may be made using any pair of refractory elements determined in this work.

figure 8



The relationship between Ti and Zr in howardites and eucrites.

figure 9



The relationship between Ba and Sr in howardites and eucrites.

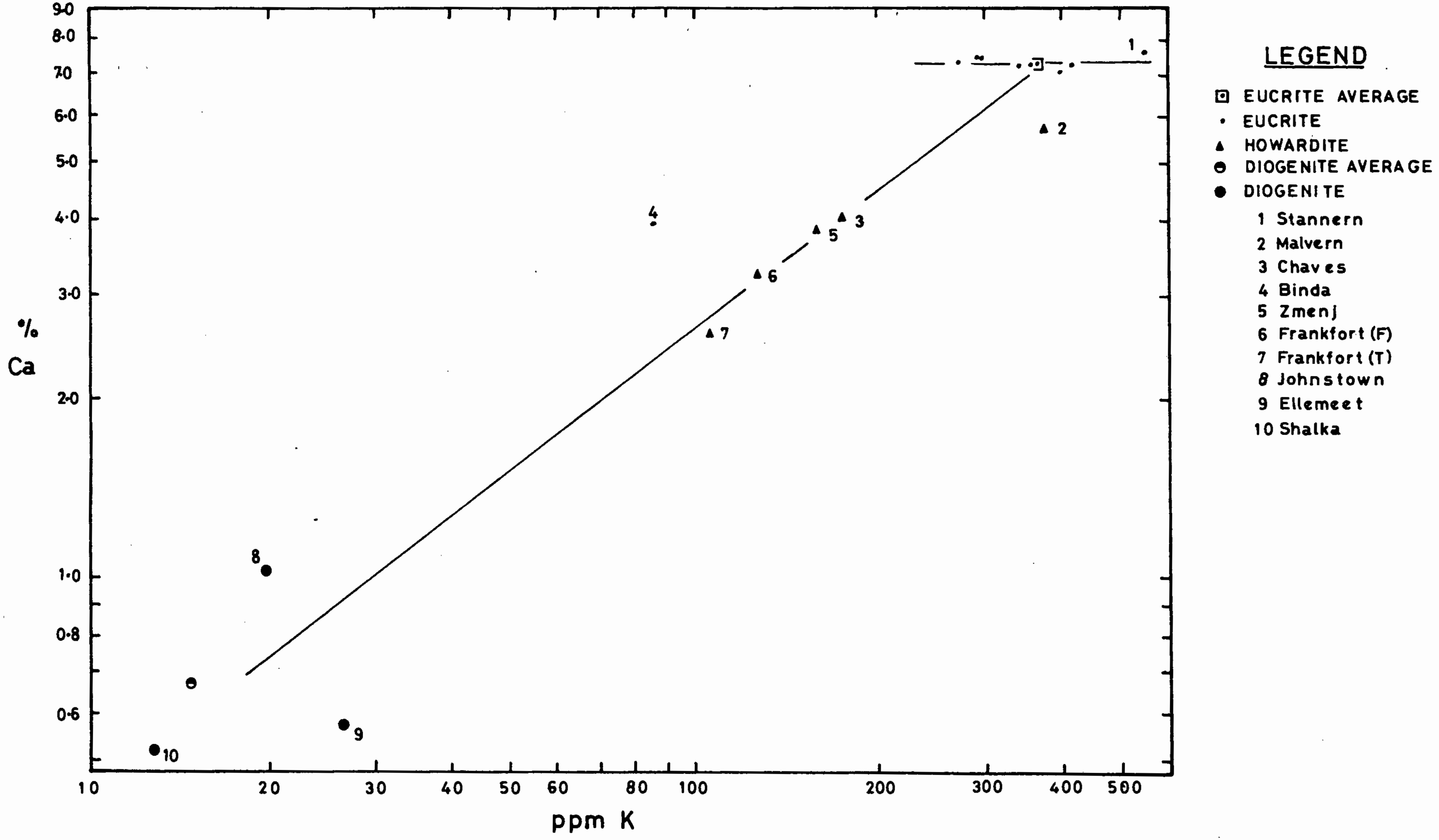
(b) Relationships between refractory and non-refractory elements.

Inter-element relationships of some importance occur within this group.

(i) The K-Ca relationship: The alkali metals, although not normally considered to be volatile elements, are nevertheless very slightly depleted in common chondrites relative to Cc_1 chondrites, and are regarded as "normally depleted" elements. (Larimer 1967, Larimer and Anders 1967). In contrast, the alkali metals(other than Li which shows a reverse tendency - Tera et al (1970)) are strongly depleted in achondrites relative to Cc_1 chondrites (Gast 1960, Larimer and Anders 1967). Explanations for this are varied, ranging from selective volatilization to mixing of different proportions of volatile-rich and volatile-depleted fractions. Irrespective of the mechanism responsible, a relationship between refractory Ca and the relatively volatile alkali metals is of interest from the point of view of the origin of the meteorite types under discussion. K has been selected for this purpose, because K data presented in this work are considered to be superior to that for Na, the only other alkali metal determined.

Data for K reported in this work are shown plotted against Ca in Figure 10. Unfortunately, few howardite data points are available. Nevertheless, a linear trend of increasing K with increasing Ca is evident. Malvern appears to be enriched in K relative to the remaining howardites - perhaps the result of contamination, as this meteorite is normal in other respects. Binda, on the other hand, is completely anomalous. Diogenites show a variation in K which is apparently random. Eucrites exhibit a range in K, reaching maximium enrichment in Stannern, a feature which was observed in discussion of refractory element behaviour. The contrast between the trend of increasing K in eucrites

figure 10



The relationship between Ca and K in diogenites, howardites and eucrites.

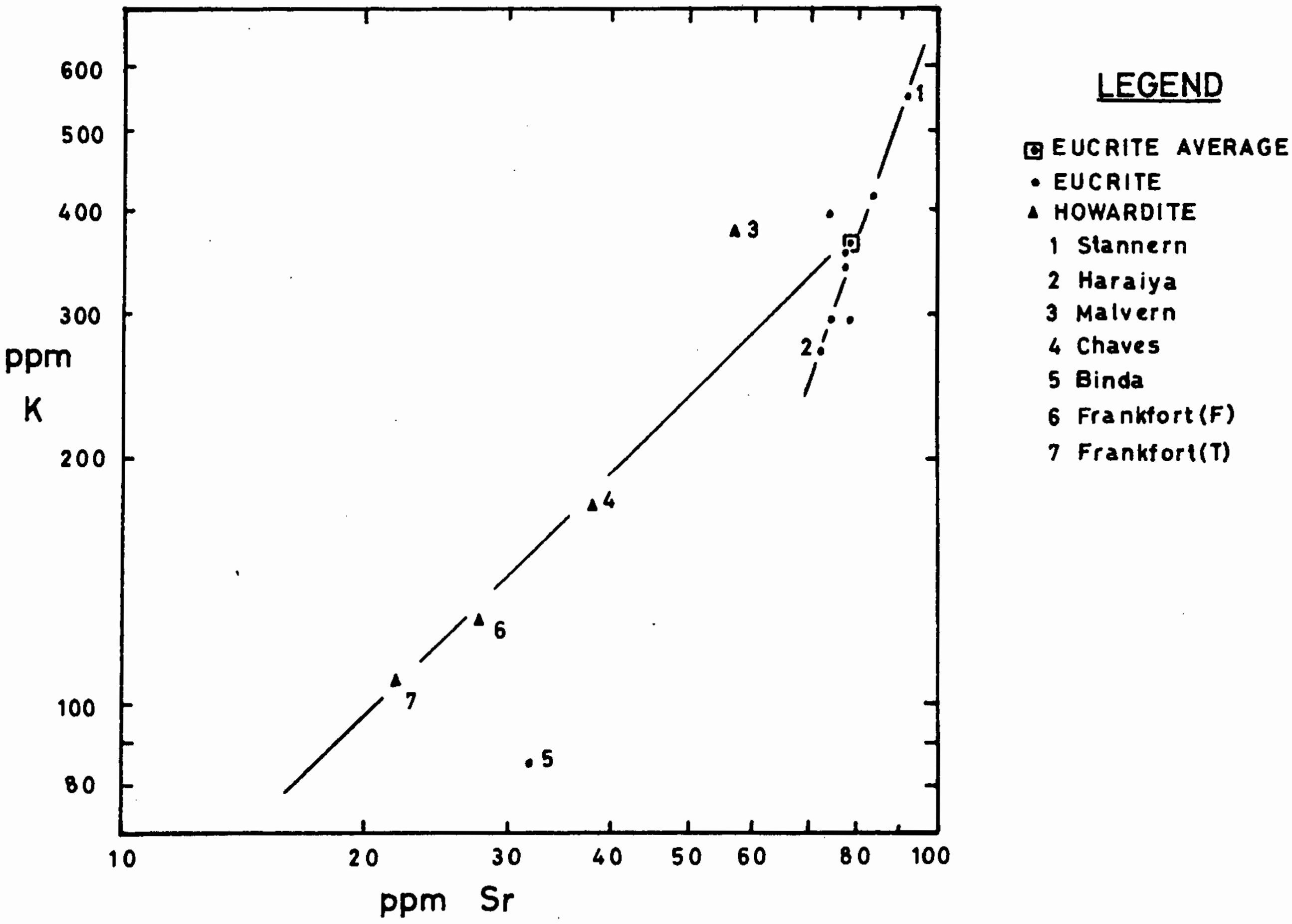
and in howardites (i.e. different slopes) is immediately obvious.

(ii) <u>The K-Sr relationship:</u> This relations is is shown in Figure 11. In howardites, there is a parallel increase in K and Sr, as would be expected from the above discussion. Eucrites exhibit this trend as well, although the two trends are distinctly different. Malvern is again suggestive of K contamination.

A similar situation would obtain if Na had been used rather than K, as may be seen if the data in Table 17 is examined. The apparently similar behaviour of these two alkali metals and refractory elements is regarded as highly significant to the understanding of processes operative during the formation of these meteorites.

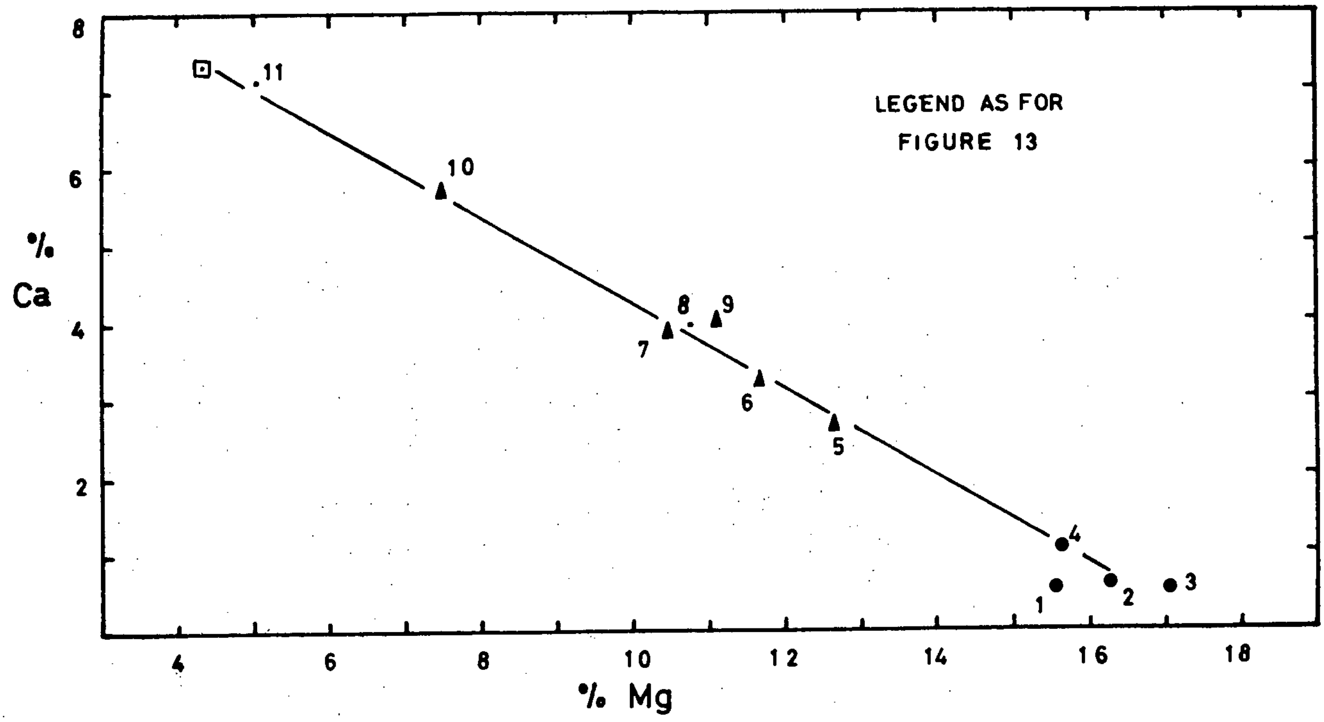
(iii) <u>The Ca-Mg relationship:</u> The inverse Ca-Mg relationship in howardites and eucrites has been noted by Ahrens and von Michaelis (1969b). A plot of Ca versus Mg for the data presented in this work is shown in Figure 12. This inverse relationship is in direct contrast to those which exist between refractory elements. It is clear that howardites form an almost continuous link between diogenites on the one hand and eucrites on the other. It will be noticed that most eucrites are of uniform composition with respect to Ca and Mg. Macibini, a eucrite, shows certain affinities with the howardites, as does the diogenite Johnstown. The unique chemistry of Binda is not revealed by the Ca-Mg relationship, and it could, on this basis, be classed as a howardite. Chaves, on the other hand, deviates from the trend line although as far as the refractory elements are concerned, it appears to be a normal howardite. Non-representative sampling could be responsible. Also significant is the fact that the two samples of Frankfort again may be seen to behave as two normal howardites, as both lie on the trend defined by the other howardites, eucrites and diogenites.

figure 11



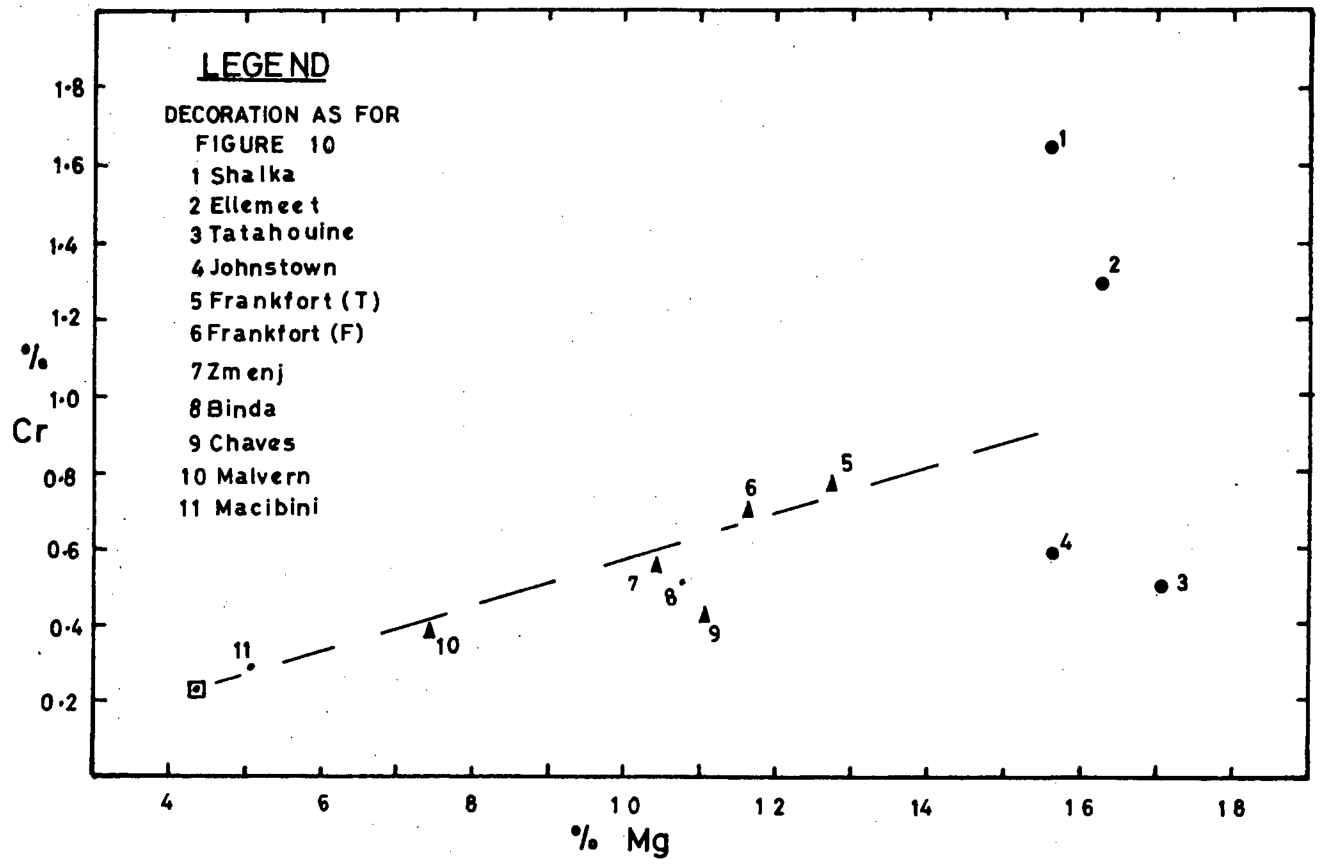
The relationship between K and Sr in howardites and eucrites.

figure 12



The Ca-Mg relationship in diogenites, howardites and eucrites.

figure 13



The Cr-Mg relationship in diogenites, howardites and eucrites.

(c) Relationship between non-refractory elements -the Mg-Cr relationship.

Ahrens (1970a) and Willis et al (1971) have observed a positive correlation between Mg and Cr in howardites. Data for these elements obtained in this work are shown plotted against each other in Figure 13. This relationship is not particularly well developed, although a trend of increasing Cr with Mg is evident. Both Binda and Chaves lie significantly off the line of increasing Cr and Mg. Significantly, both samples of Frankfort lie on a line between the diogenite average and the average eucrite. Macibini again may be seen to show howarditic affinities. Diogenites are extremely variable with respect to Cr. This may reflect the random distribution of the chromite in these meteorites, although it would appear from analyses of hypersthene (or more correctly, bronzite - Keil 1969a) from Johnstown and Tatahouine presented by Mason (1963a) that this mineral contains considerable quantities of Cr. Unfortunately, most analyses of diogenites by other workers are rather old, making assessment of the sample to sample variability impossible. (See Mason 1963a).

2. Consideration of Fe, Si and Mn abundance.

In their study of achondrite chemistry, Ahrens and von Michaelis (1969b) and Ahrens and Danchin (1971) pointed out that these three elements remained constant in howardites and eucrites, in spite of rather large variations in composition among the howardites. As discussed previously, slight fractionation of Fe and Si was observed between howardites and eucrites in the data presented in this work. The fractionation of these two elements is not discrete, but appears to be related to the general composition variations in howardites discussed above. Using Ca as a measure of the composition variation in howardites, both Fe and Si may be seen to vary somewhat regularly with this parameter. (Figures 14 and 15 respectively). The scatter of points is large, but the regular variation with Ca particularly for Si is clear. Also apparent in these figures is the fact that diogenites again form an end member in the howardite sequence, as was observed above for other elements. Nevertheless, over the whole sequence from eucrite to diogenite, Fe decreases by only 2%, while Si increases by a similar amount. In contrast, Mn is present at the same abundance level in eucrites, howardites and diogenites, as isshown diagramatically in Figure 16. A decrease in Mn with decreasing Ca may exist, but in view of the scatter of data points, this cannot be established with any certainty.

3. Relationships involving the FeO/(FeO + MgO) ratio.

This ratio is widely used as an index of igneous differentiation, based on the fact that Fe enriches in ferromagnesian minerals as differentiation proceeds. Accordingly, it has been applied to achondrite studies as well, e.g. Mason (1967). From considerations of the data presented in this work, it is clear that this ratio, if calculated from a meteorite analysis, will show a regular increase from diogenites to eucrites, since Fe varies only between narrow limits, while Mg shows considerable variation over the same range. Thus, the FeO/(FeO + MgO) ratio is,at the first approximation, equivalent to the reciprocal of the Mg abundance and the positive correlation between CaO and FeO/(FeO + MgO) in diogenites, howardites and eucrites reported by Mason (1967) is equivalent to a plot of CaO against 1/MgO. It follows that all trace elements discussed here which show enrichments or depletions corresponding to the Mg composition range will correlate with the FeO/(FeO + MgO) ratio.

figure 14

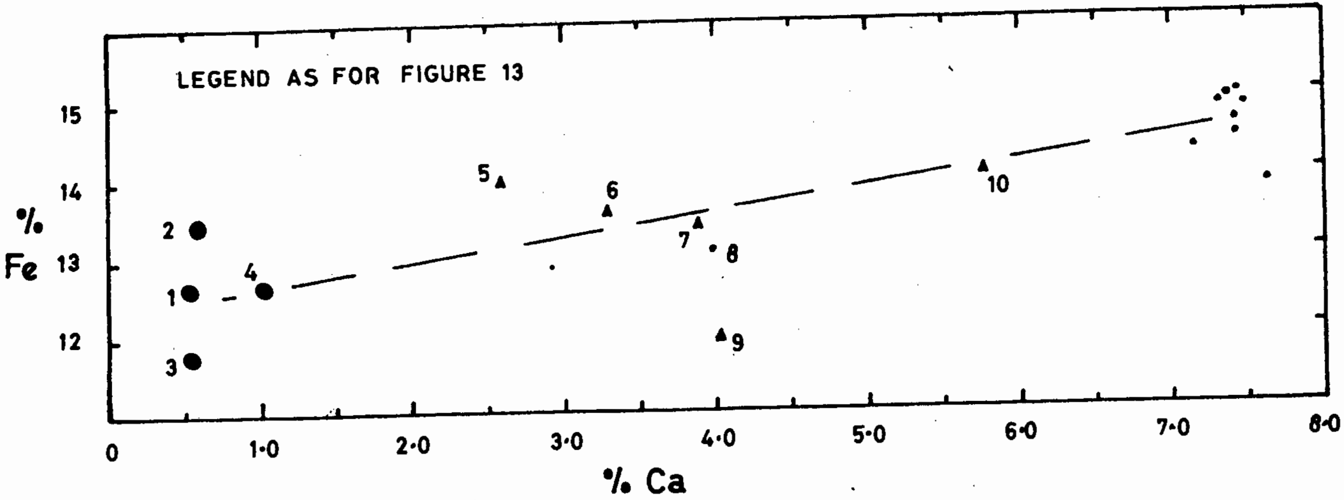


figure 15

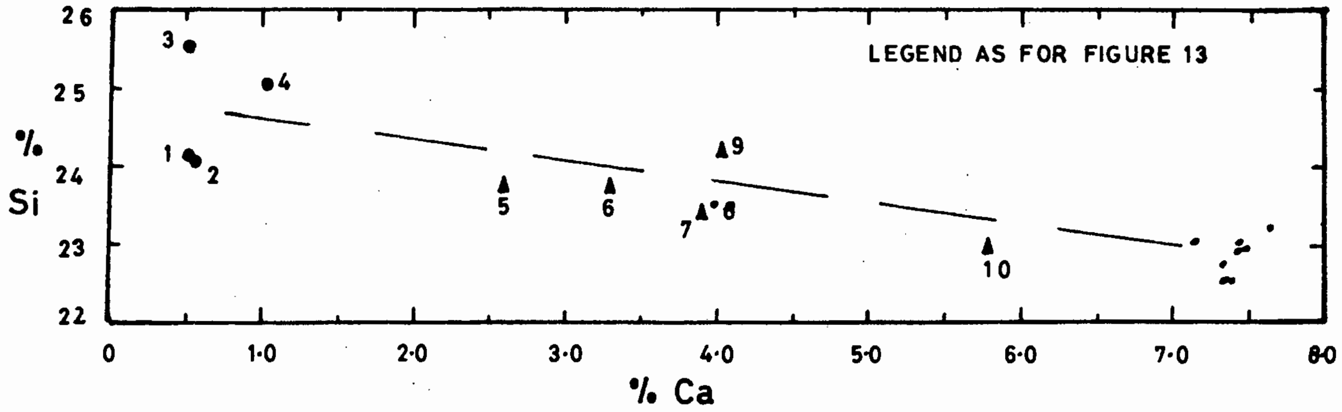
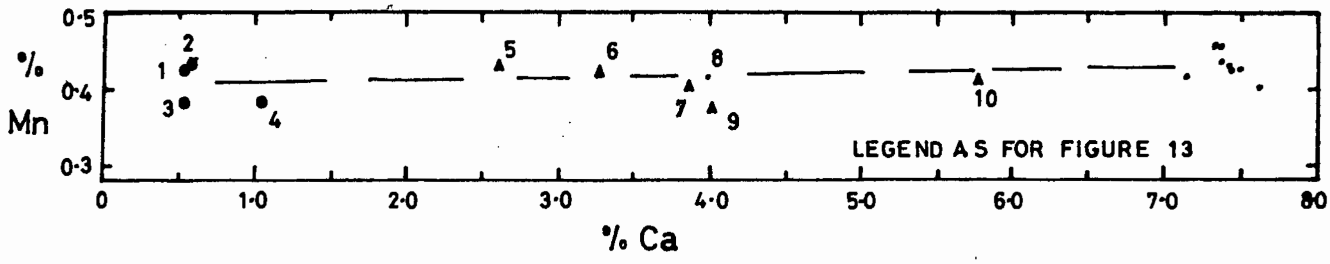


figure 16



The relationship between Ca and Fe, Si and Mn in diogenites, howardites and eucrites.

4. The significance of inter-element relationships in consideration of the origin of the howardites.

It is proposed here to review some theories put forward for the origin of diogenites, howardites and eucrites in the light of the element abundance relationships discussed above.

(a) Igneous differentiation model.

This model is widely accepted at the present time to account for trends in major element composition exhibited mainly by the howardites. The continuous spectrum of composition fromdiogenites through howardites to eucrites was attributed by Moore (1962) to fractionation in a silicate melt. The sequence of minerals crystallizing from this melt (possibly a carbonaceous chondrite - Moore 1962) was olivine and hypersthene (bronzite) to form the diogenites (Roda and Ellemeet are known to contain olivine, - Mason 1963a). The appearance of plagioclase simultaneously with pyroxene on the liquidus resulted in howardite formation. As this differentiation proceeded, the orthopyroxene crystallization was superseded by clinopyroxene, and the eucrites began to form. This model has been adopted by Mason (1962), but pallasites have been included as an early differentiate, following the suggestion of Ringwood (1961) that the parent material was a common chondrite. More recently, Mason (1967) has again discussed this mechanism with some refinements, but with few major changes. He suggested H group chondrites as a possible parent material.

The inter-element relationships exhibited by the major elements discussed here place certain restrictions on this model, the more important of which will now be considered. Perhaps the most significant is the Ca/Al ratio, which remains almost constant over the whole range of known eucrite and howardite composition (i.e. from Frankfort to Stannern). This ratio is significantly greater than the maximium possible in plagioclase (1.10 as opposed to 0.74). The additional Ca required to satisfy this ratio is presumably located in the clinopyroxene, the only other major Ca bearing phase in these meteorites. (Mason 1967, Duke and Silver 1967). In order to maintain the Ca/Al ratio at its observed value, the relative proportions of plagioclase and clinopyroxene crystallizing at any one instant must be carefully balanced (orthopyroxene and olivine can be effectively considered as diluents). This balance must remain over the entire composition range from Frankfort to Stannern. In addition the Ca-Mg relationship poses further restrictions on the model. The bulk of the Ca in the howardites and eucrites probably occurs in plagioclase, while Mg occurs in both ortho- and clinopyroxene. In order to generate the inverse trend observed between Mg and Ca, the relative proportions of orthopyroxene and plagioclase crystallizing must be inversely related. Clinopyroxene, also a major Mg - bearing phase, must however of necessity follow plagioclase in order to maintain the Ca/Al ratio, as mentioned above. In addition, the Fe content of the meteorites involved varies only slightly,in contrast to the large variation in Mg. Thus, parallel to the trend of decreasing Mg, Fe content of the ferromagnesian minerals would have to increase in order to maintain constant Fe. The overall picture is one of a very delicate balance of mineral proportions, over a considerable range of differentiation. It is difficult to imagine igneous differentiation operating in such a perfectly balanced way, although of course, this is not conclusive evidence. One could envisage this balance operating, since relative proportions of minerals crystallizing are controlled by the melt composition and by pressure and temperature conditions prevailing during crystallization.

Considerations of trace elements are also important. The various inter-element relationships among trace elements discussed previously suggest that two separate processes have been involved in the formation of eucrites and howardites respectively, as these meteorites each define a separate trend in trace element distribution. In spite of the scatter of the data for howardites, it appears that these processes were not sequential, i.e. processes forming the eucrites did not'follow on'from those forming the howardites. No reasonable explanation can be provided for this in terms of a simple igneous differentiation model, as the only mineralogical differences which exists between howardites and eucrites according to Mason(1967) is the dominance of clinopyroxene over orthopyroxene in eucrites, while the reverse is true in howardites. A change in mineralogy of this nature during differentiation is not likely to produce such marked differences in the trace element distribution observed in this work between howardites and eucrites.

From these considerations, it seems unlikely that a process of igneous differentiation could have sequentially produced the diogenites, howardites and culminated in eucrite formation. This does not, of course, rule out the possibility of some process of igneous differentiation having operated within individual groups. The study of Moore County by Hess and Henderson (1949), for example, is unequivocal proof that these processes have been involved in the formation of some of these meteorites. The implication of this discussion is that the variations in major element composition observed in the howardites are not the result of igneous differentiation. It will be shown that this process was probably largely responsible for diogenite and eucrite formation.

(b) Sequential condensation model.

Following the work of Ahrens and von Michaelis (1969a,b), it appeared that the Ca/Al ratio was identical between howardites, eucrites and chondrites. This, coupled with the Ca/Mg and the almost constant Fe content, indicated that igneous differentiation of a chondritic parent material was unlikely as the mechanism of formation of the chemical variations in howardites and eucrites (Ahrens and von Michaelis 1969b). The similar Ca/Al ratio in chondrites, howardites and eucrites led von Michaelis (1969) (and the author) to believe that howardites and eucrites were formed by sequential condensation from the nebula at high temperature. The general enrichment in refractory elements in eucrites relative to chondrites supported this view, as did depletion in alkali metals (Li excluded). Further, Larimer (1967) has calculated condensation temperatures of some compounds likely to form in the nebula. It is significant that those compounds formed at extremely high temperatures contain Ca, Al and Ti. The revision of these condensation temperatures by Larimer and Anders (1970) indicated that Fe metal condenses at temperatures considerably lower than these refractory elements. The low metal (and alkali) content of the howardites and eucrites could thus be explained by the isolation of the early-formed condensate before the bulk of the Fe metal and alkali metals condensed. This model breaks down under detailed scrutiny of alkali abundances relative to refractory elements. It has been shown in this work that K and Na show a parallel increase with Ca through the howardite sequence. K and the refractory elements also show a parallel increase in abundance in eucrites. In terms of this model, K should decrease with increasing Ca, assuming the relative condensation temperatures of Larimer (1967) are correct.

Although this model does not hold in detail, it may nevertheless provide an explanation of the origin of the parent material from which diogenites, howardites and eucrites subsequently formed.

(c) Mixing Model.

Recently, Jérome and Goles (1970) proposed a mixing model to account for the observed chemical variations amongst the howardites. These authors point out that the main evidence for this is based on petrographic studies, although the features produced are observable in the chemistry of the howardites. It will be recalled that Duke and Silver (1967) observed that most howardites are polymict breccias, containing 'fragments with a wide variety of magmatic and crystallization texture....'. This remark has been expanded by Jérome and Goles (1970), who suggest that the howardites represent various proportions of mixing of eucrites and diogenites, brought about during the fragmentation of the original parent body. The Ca-Mg relationship is used by these authors to show the continuous sequence in composition through the howardites from eucrites at the one extreme to howardites at the other.

Further chemical evidence for this model is provided by the data presented in this work. It will be recalled that the Ca/Al ratio of howardites shows slight but significant deviations from the chondritic value with decreasing Ca content (Table 41 and Figure 5). In terms of the mixing model, deviation towards a higher Ca/Al ratio is brought about by increasing proportions of diogenite in the mixture, which has a Ca/Al ratio significantly higher than that of chondrites. The abundance of Fe, Si and Mn, as discussed previously, also lend support to the mixing model. The Si content of howardites is seen (Figure 15) to decrease as the proportion of eucrite, as measured by the Ca content, increases. The reverse is true for Fe. Mn, on the other hand, is present in similar abundance in both diogenites and eucrites, so that this element remains at a virtually constant level of abundance in howardites.

The differences in bulk composition between the two samples of Frankfort analysed in this work also provide further compelling evidence in support of a mixing model. Frankfort (F) consisted of 5.3 g of fragments, ranging in size from powder to about 05 mm chips. Frankfort (T) was received as a single slice weighing 9.4 g. Examination of the hand specimens showed obvious differences. Frankfort (T) consisted of fine-grained, grey material, similar in appearence to other howardites. Set in this material was a single large pyroxene fragment, as shown in Plate I.7

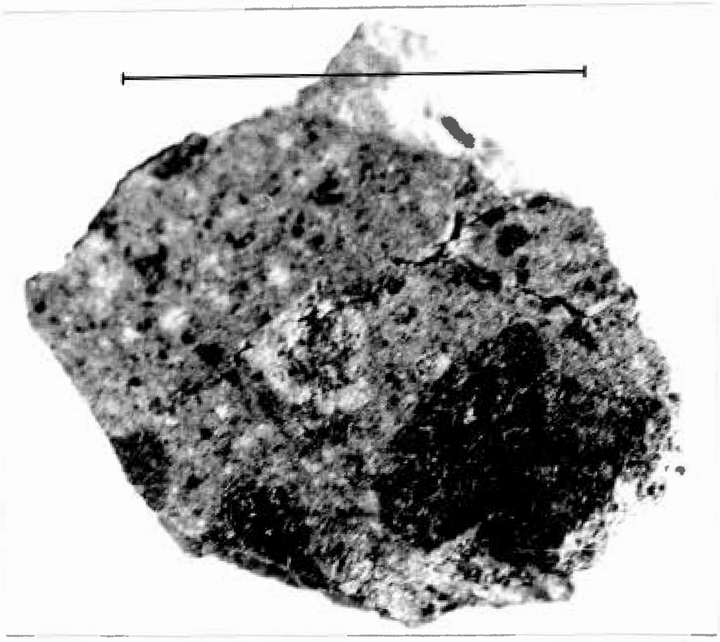


PLATE I

Frankfort (T). The scale bar is 2cm in length.

Frankfort (F) appeared similar to the matrix material of this sample. The differences in chemical composition observed between the two samples are thus most probably due to the presence of this large pyroxene crystal in Frankfort (T). It is significant that in each of the element pairs considered in the above discussion on inter-element relationships, both samples of Frankfort are seen to lie on the line between eucrites and diogenites and that Frankfort (T) always lies closer to the diogenites than Frankfort (F). Using an average diogenite and an average eucrite calculated from the data presented in this work, it is possible to reconstruct both samples simply by using different proportions of diogenite and eucrite. The results of these calculations are presented in Table 42 and indicate that differences in composition between the two Frankfort samples could have arisen through the presence of 8 % more diogenite in Frankfort (T). The agreement is good between measured and calculated abundances, particularly for the important elements Mg, Ca and Al. The largest discrepancies occur for Fe, K and Si. Reference to Table 17 and Figures 10, 15 and 16 indicates that diogenites and eucrites, but particularly diogenites, are somewhat variable with respect to these elements, so some error is likely to occur if simply an average end member is used. In order to obtain a perfect fit for all elements, the exact end member material would have to be discovered. This is particularly true for trace elements, which show considerable variations in diogenites and eucrites.

TABLE 42

Reconstruction of Frankfort.

	Average Eucrite	Average Diogenite
Fe %	14.58	12.62
Mn %	0.434	0.409
Ti %	0.417	0.046
Ca %	7.38	0.67
Cr %	0.23	1.01
P %	0.042	0.003
Si %	22.88	24.69
Al %	6.66	0.43
Mg %	4.32	16.11
Na %	0.39	0.04
K ppm	364	15

TABLE 42 (cont.)

	38%eucrite+ 62%diogenite	Frankfort (F)	30%eucrite+ 70%diogenite	Frankfort (T)
Fe %	13.36	13.50	13.20	13.91
Mn %	0.419	0.427	0.420	0.430
Ti %	0.187	0.170	0.157	0.136
Ca %	3.22	3.28	2.68	2.60
Cr %	0.72	0.69	0.78	0.76
P %	0.018	0.020	0.015	0.015
Si %	24.00	23.78	24.14	23.79
Al %	2.80	2.88	2.30	2.26
Mg %	11.63	11.63	12.58	12.63
Na %	0.17	0.15	0.15	0.16
K ppm	148	128	120	108

Calculations similar to this have been done by Jérome and Goles (1970) for different howardites, and they report good agreement for most elements. The reconstruction of the Frankfort samples given above illustrates such agreement. This example is particularly interesting however, in that two samples of a single meteorite are involved.

The data presented in this work clearly support a mixing model for the origin of the polymict howardites. One of the two processes recognisable in trace element distribution in howardites and eucrites is satisfactorily explained by this mechanism. The inter-element relationships raised in this work as objections against the igneous differentiation model find an explanation in the mixing model as well. The balance between the major Ca bearing minerals, plagioclase and clinopyroxene, required to maintain the Ca/Al ratio is satisfied by a mixing process where the relative proportions of these minerals found in eucrites remain unchanged in howardites. The inverse Ca/Mg results from dilution of a eucrite with Mg rich bronzite.

5. Further discussion on the mixing model.

The mixing model proposed by Jérome and Goles for howardite origin seems to be in full accordance with the data presented here. Further details of this mixing process will now be discussed.

(a) End-member composition.

In the reconstruction of the Frankfort samples discussed above, it was apparent that the use of average diogenite and eucrite end members did not quite produce perfect agreement for all elements. Thus, for instance, in Figures 14, 15 and 16 howardites do not all lie on the ideal mixing line joining the eucrite and diogenite averages. In addition, it was noted in the discussion on the trace element inter-relationships that the scatter of howardite points about the fitted lines was considerably greater than that for eucrites. This is interpretted as indicating that no single eucrite or diogenite type dominated over others in its contribution to the mixing process. Thus, the sample of Zmenj analysed for REE by Schnetzler and Philpotts (1968) was found to have a small, negative europium anomaly, indicating admixture of eucritic material similar to Stannern. The howardite Bununu, by contrast, did not exhibit any europium anomaly, and its eucritic component was probably similar to Juvinas. (Stannern has been shown to possess a marked Eu anomaly, while Juvinas shows normal relative Eu abundance - Schnetzler and Philpotts 1968).

The variable nature of the eucritic component in howardites studied in this work is indicated by the Ba/Sr ratio. As both these elements are present in amounts less than 2ppm in diogenites, the ratio of the eucritic component is likely to dominate the ratio of the mixture (i.e. howardite) over quite a considerable Ca range. The Ba/Sr ratio of the eucrites studied in this work varies from 0.35 in Haraiya to 0.55 in Stannern, and that of the howardites from 0.36 to 0.49. It would appear that the howardites examined in this study contain representatives of almost the entire spectrum of eucrite composition.

In the case of the diogenites, however, the situation appears to be slightly different. If the diogenite samples analysed in this work are representative with respect to Cr, it would appear from Figure 13 that those diogenites low in Cr are represented in the howardites studied in this work, while the high Cr diogenites are most certainly not. However, before a firm conclusion can be drawn in this regard, more analyses of diogenites are required in order to establish the distribution of Cr in these meteorites. The Cr data collected by Ahrens and Danchin (1971) also suggest that the high Cr diogenites are not well represented in the howardites.

Jérome and Goles (1970) suggested that some chondritic material may be present in howardites in addition to diogenitic and eucritic material, in order to account for excesses in Na, P, Fe, Ni, Co and Cu which were found when calculated compositions of howardites were compared with the measured compositions. In view of the difficulty of specifing the composition of the diogenitic and eucritic end members exactly, this problem of excess Na and Fe and other siderophile elements is difficult to assess. Further, non-representative sampling with respect to the metal phase could quite conceivably lead to excesses in siderophile elements. In general, no inexplicable excesses in these elements were observed in this work, suggesting that a chondritic component might not be as widespread as Jérome and Goles (1970) imply.

(b) Implications of the mixing model on achondrite classification.

The implications of the mixing model on achondrite classification have been discussed by Jérome and Goles

(1970). Some of their more important observations will be restated here together with some implications which have arisen from this work. The concept of a Ca-rich and a Ca-poor achondrite variety is no longer tenable, as a complete spectrum of composition is possible in terms of this model. In fact, Johnstown, long regarded as a diogenite, does show certain affinities with howardites. Similarly, Macibini, a eucrite, also shows howarditic affinities. Probably the most suitable criterion for the classification of eucrites and howardites (and, presumably, the diogenites) available at the present time is that proposed by Duke and Silver (1967), i.e. the nature of the brecciated structure. This classificatiom has been adopted in this work as it is considered to be genetically more meaningful than the simple mineralogical classification of Mason (1967), since it recognizes the howardites as the product of mixing of other meteorite types. In terms of Duke and Silver's classification, Binda, a monomict breccia (Duke and Silver 1967), is classified as a eucrite, although its bulk chemistry is similar to many howardites. Binda nevertheless differs from howardites in terms of trace element inter-relationships, as seen in the discussion on these relationships. The fact that Binda is a monomict breccia suggests that it had a different genesis to the polymict howardites. This is further substantiated by trace element inter-relationships. It is clear from these relationships that the monomict nature of Binda is not a secondary feature - i.e. recrystallization of a polymict breccia followed by brecciation, but rather relates to the fact that it has escaped the mixing process. Binda is regarded as a eucrite for the purposes of this work simply to indicate that it originated in a different way to howardites, in spite of the fact that, as far as its bulk composition is concerned, Binda shows closer affinities with howardites than with eucrites. In fact, Binda does create something of a dilemma for the classification system, since Binda is no more a eucrite than a diogenite in terms of its bulk chemistry, and thus, strictly speaking, should form a class on its own.

(c) Implications of the mixing model on diogenite - eucrite association.

As discussed previously, it would seem that representatives of almost the entire range of eucrite composition go to make up the the howardites. As far as the diogenitic component is concerned, there may be a greater proportion of low Cr representatives, although this is not certain. Further, an almost complete gradation exists between the two end members indicating a complete range of mixing proportions. Although many such mixtures of meteorite types are known (see, for example, Lovering 1962, Wahl 1952, Binns 1967a and 1968a), only howardites and the silicate fraction of the possibly related mesosiderites (Lovering 1962, Duke and Silver 1967, Jérome and Goles 1970, Powell 1971) show such a wide range of mixing proportions. It is thus reasonable to conclude that diogenites and eucrites were related in a single parent body. During the fragmentation of this body, a complete range of mixing of all possible types of diogenite and eucrite occurred. That eucrites and howardites, and diogenites probably originated in close proximity is bourne out by the age studies of Heymann et al (1968) and Ganapathy and Anders (1969).

The extent of mixing which has occurred within the diogenites and eucrites themselves is difficult to estimate. Such mixing might be difficult to detect, in view of the limited composition range represented by the eucrites and diogenites. However, Duke and Silver (1967) have recognized distinct textural types within the eucrites, and they state that ' in a specific eucrite the lithic fragments have essentially identical mineral compositions and a limited textural variety '. Cross mixing amongst eucrites at least, seems to be minimal.

6. The significance of inter-element relationships in considerations of the origin of diogenites and eucrites.

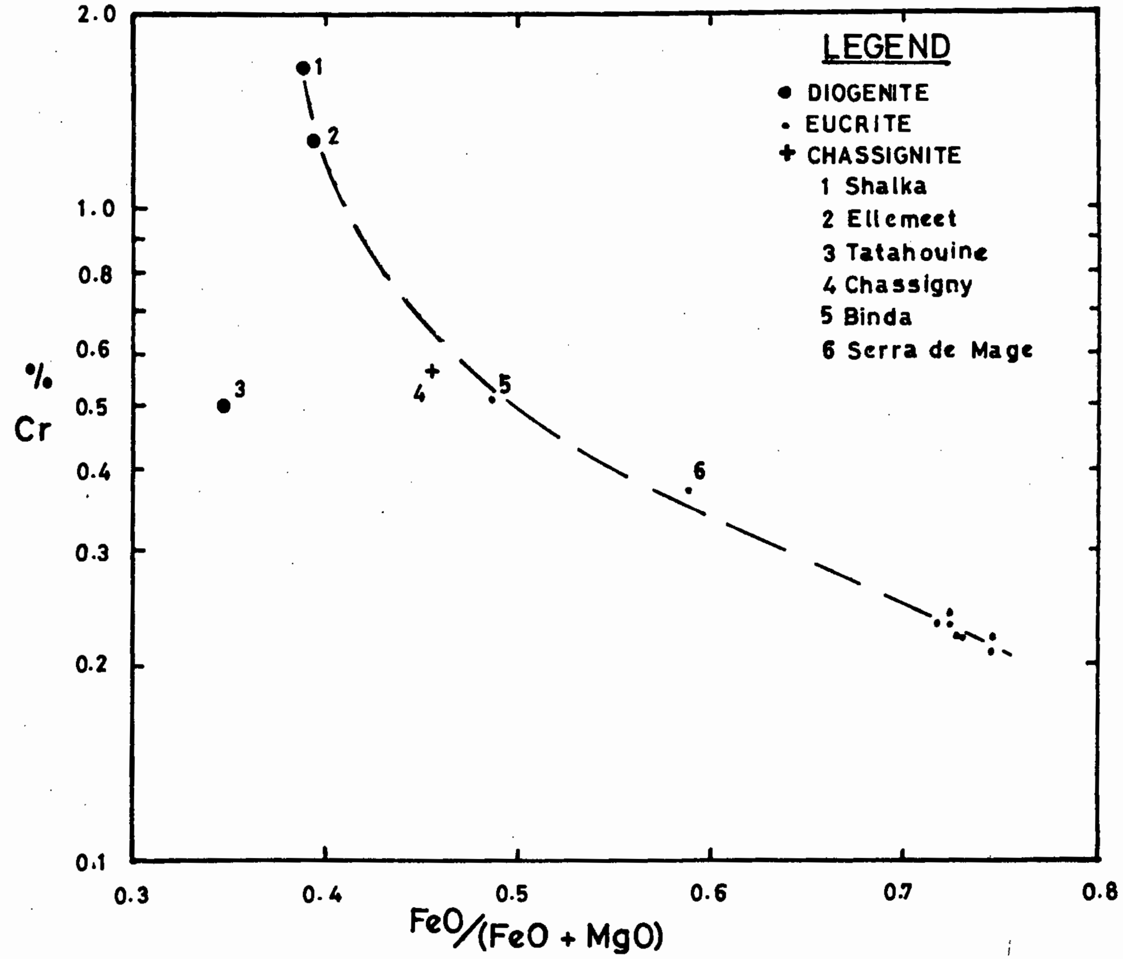
It has been shown that howardites were formed by the mixing of diogenites and eucrites. It is now proposed to discuss the origin of these latter two meteorite types. As far as the origin of eucrites is concerned, the consensus of opinion seems to favour crystallization from a melt. This theory is supported in detail by crystal orientation (Hess and Henderson 1949, Duke and Silver 1967), REE distribution (Schnetzler and Philpotts 1968) and crystallization texture (Duke and Silver 1967).

In the igneous differentiation model proposed by Mason (1962, 1963a, 1967) for the origin of diogenites and eucrites, howardites formed a convenient bridge across the chemical hiatus between diogenites on the one hand and eucrites on the other. In terms of the mixing model, howardites can no longer be regarded as such. It is therefore necessary to review the evidence for a common origin of diogenites and eucrites.
As discussed in the previous section, howardites represent virtually a complete range of mixing proportions of diogenites and eucrites. In view of this it was concluded that diogenites and eucrites originated in fairly close proximity. Further evidence for a related origin is their similar oxygen isotope chemistry as observed by Taylor et al (1965). The existence of a pyroxene rich material as an early-formed phase is not unexpected in the differentiation which produced the eucrites. Duke and Silver (1967) pointed out that crystallization probably began in the pyroxene field of the system plagioclase - pyroxene. On this basis it would appear that the two types are genetically related.

Unfortunately, no unequivocal chemical link exists between the two groups. Binda, a monomict breccia (Duke and Silver 1967), has a composition intermediate between diogenites and eucrites and, as far as the author is aware, represents the only unambiguous chemical link between the two. It is quite possible that other meteorites occupying a similar position to Binda in the differentiation sequence have been converted to polymict breccias during the break-up of the parent body. Before any details of the supposed differentiation sequence can be discussed, it is essential that the representatives of this sequence be recognized. Binda is regarded as a member of this sequence because of its brecciated structure and on the basis of trace element inter-relationships. Macibini has been excluded, as it shows affinities with the howardites. All remaining eucrites which have been analysed in this work are regarded as monomict, and therefore considered to be differentiates. Similarly, the diogenites, excluding Johnstown which shows howarditic affinities, have been included as well.

(a) The parameter $FeO/(FeO+MgO)$: Assuming that the range of rock types represented in each monomict brecciated meteorite is small, then clearly the parameter $FeO/(FeO+MgO)$ calculated from the chemical analysis of a eucrite or diogenite is a valid index of differentiation. A regular relationship appears to exist between this ratio and Cr (if Tatahouine is ignored), as is shown in Figure 17, in the form of a distinct drop in Cr with increasing $FeO/(FeO+MgO)$ ratio. This relationship/is common in basic igneous differentiates (e.g. Curtis 1964) similar to the diogenite - eucrite suite. Elements such as the alkali metals and alkaline earths, Y, Zr, Sr, Ba, etc. enrich as the $FeO/(FeO+MgO)$ ratio increases, as would be expected in a differentiation sequence. Other than for showing these broad trends, however, the ratio $FeO/(FeO+MgO)$ is of little practical use in this study, because it is too insensitive to enable its use in the most populated part of the differentiation sequence, viz. amongst the eucrites.

figure 17



The relationship between the FeO/(FeO+MgO) ratio and Cr in diogenites and eucrites.

(b) Trace elements: These provide a far more sensitive means of examining the crystallization history of the eucrites. Unfortunately, the important elements Sr, Y, Zr and Ba could not be measured in the diogenites because of the limitations of the X-ray fluoresence technique. Nevertheless, Binda and the remaining eucrites show sufficient variation in these trace elements to throw some light on conditions prevailing during the formation of diogenites and eucrites.

(i) Order of crystallization of eucrites and diogenites studied: In terms of gross chemical features such as the FeO/(FeO+MgO) ratio, the order of crystallization appears to be identical to that suggested by Mason (1962, 1963a, 1967), viz. firstly diogenites, followed by Binda and then eucrites in general (howardites are, of course, excluded). As mentioned, no representatives are known immediately before and after Binda (Figure 17). These hiatuses may reflect distinct layering within the parent body, as is common in basic intrusions on earth, e.g. Bushveld and Stillwater complexes. However, in view of the magnitude of the hiatuses in FeO/(FeO+MgO), it seems more likely that some representatives must exist to fill these gaps. This is discussed at greater length below.

Amongst the diogenites, crystallization probably followed the order Tatahouine - Shalka - Ellemeet, judging by the Na and K contents, which increase in this order. This is supported by the FeO/(FeO+MgO) ratio, and, at least in part by the Cr abundance (Figure 17). It is rather intriguing that Tatahouine is unique among diogenites in that it displays local recrystallization, which Mason (1963a) has attributed to 'mechanical deformation' under extreme confining pressure. Another interesting feature concerning these meteorites is the absence of olivine from both Tatahouine and Shalka, and its presence in Ellemeet. This has some bearing on the postulated genetic association of pallasitic meteorites with diogenites (Ringwood 1961, Mason 1962, 1967).

These authors have suggested that crystallization of pallasites, diogenites and eucrites took place in this order from a melt of L or H group composition. It seems remarkable, however, that the earliest formed member of the diogenites contains no olivine (Tatahouine or Shalka), while later formed members (e.g. Ellemeet) do. Further, the olivine in pallasites contains very little Cr (Mason 1963b), inconsistent with their derivation from the same melt prior to the diogenites. The unique achondrite Chassigny might be related to the diogenites as well, as this meteorite is composed essentially of olivine with some feldspar (Fabries, pers. comm.). Examination of the analysis of this meteorite undertaken in this work indicates that it contains relatively large quantities of alkali metals (0.11 % Na, 268 ppm K) relative to diogenites, and thus is probably not an early differentiate of the melt which gave rise to the diogenites.

As stated previously, an hiatus appears to exist between diogenites and Binda. Some meteorites are known which could possible fall in this region, although not without some ambiguity. In terms of the FeO/(FeO+MgO) ratio, Chassigny could be a representative of this region of the crystallization sequence, i.e. it crystallized after the diogenites. Its FeO/(FeO+MgO) ratio of 0.46 falls between those of the diogenites (0.38) and Binda (0.49). Reference to Figure 17 indicates that its Cr abundance is also consistent with an origin in this portion of the sequence.

However, the K and Na contents of Chassigny are not consistent with this suggestion, although these may reflect the presence of large amounts of trapped liquid, i.e. magma which was trapped in the sample during its formation. Although Hey (1966) classifies Chassigny as an achondrite, he does state that this meteorite contains chondrules. Its role relative to the diogenites and eucrites thus remains uncertain.

As indicated previously, Binda probably crystallized before the eucrites, as indicated by Cr abundances, its FeO/(FeO+MgO) ratio and its general intermediate character with respect to Ba, Sr, Y, Zr, Na and K.

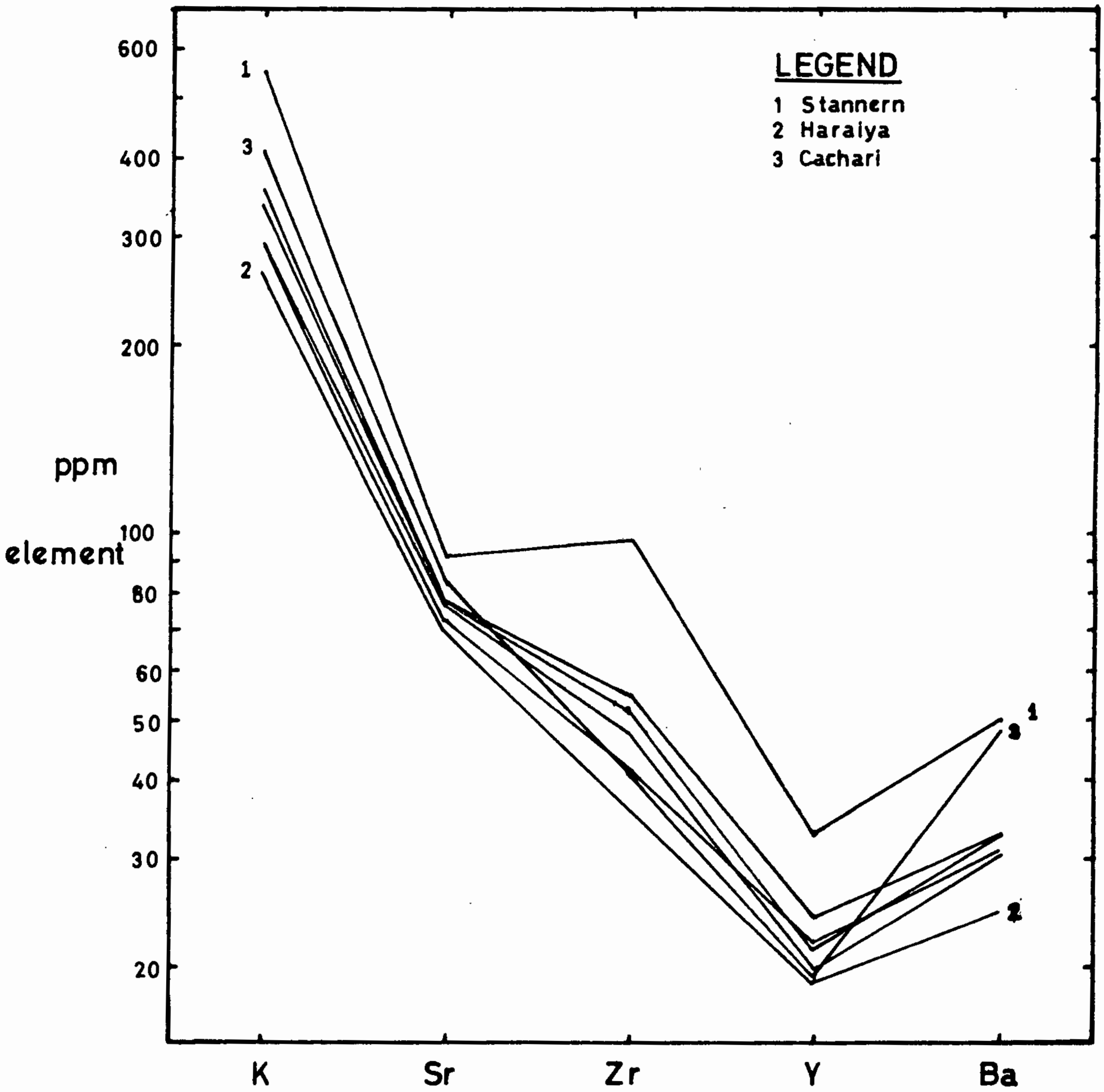
The hiatus between Binda and the eucrites likewise cannot be filled unambiguously. The somewhat unusual eucrite Serra de Mage could possibly represent material formed in this region of the differentiation sequence, judging by its FeO/(FeO+MgO) ratio of 0.59, and its Cr content (Figure 17). However, the Sr and K contents are not consistent with Serra de Mage having crystallized subsequent to Binda. The Sr/Ca and K/Ca ratios of Serra de Mage (data of this work and Schnetzler and Philpotts 1968, who analysed the same powder as the author) are 7.83 and 9.25 respectively, while those of Binda are 8.02 and 21.30 respectively. These ratios suggest that Serra de Mage crystallized from a liquid poorer in both Sr and K than Binda . For comparison, Haraiya (a eucrite) has Sr/Ca and K/Ca ratios of 9.69 and 36.83 respectively. The Ba/Ca ratio (1.17) is also consistent with the crystallization of Serra de Mage prior to Binda (Ba/Ca = 2.76). It is assumed that most of the K, Sr and Ba are in plagioclase, and that these elements increased in abundance in the liquid as differentiation proceeded. These assumptions seem reasonable, as will become apparent in later discussion. It is likely that the evidence of the Sr/Ca ratio is in general a more reliable index of relative formation times than both the FeO/(FeO+MgO) ratio and the Cr abundance. The validity of the Sr/Ca ratio is supported by various other parameters in the case of the eucrites, while in this same group of meteorites, the FeO/(FeO+MgO) ratio calculated from the bulk chemical analysis is apparently completely insensitive. On the other hand, the presence of trapped liquid in Binda, which could increase its Sr/Ca ratio, cannot be ruled out. It would appear then, that immediately prior to or following the crystallization of Binda, some plagioclase cumulates formed, the representative of which is Serra de Mage. (Schnetzler and Philpotts(1968) have pointed out that Serra de Mage is a plagioclase cumulate. A similar conclusion is reached in this work, as is shown below.)

Like Serra de Mage, Moore County is also regarded as a cumulate by Schnetzler and Philpotts (1968), who cite the work of Hess and Henderson (1949) in this regard. Using their K, Sr and Ba data, it would appear that this meteorite formed immediately prior to those eucrites studied in this work. As pointed out by Schnetzler and Philpotts, this meteorite shows evidence of some closed-system competition between pyroxene and plagioclase for trace elements, and could possibly represent liquid and settled crystals which became isolated from the main stream of differentiation.

The remaining portion of the differentiation sequence is well represented by the eucrites. Variations in major element composition through this sequence are virtually nil, suggesting that the eucrites represent sequential eutectic crystallization. Within the eucrite sequence, Duke and Silver (1967) have observed distinct textural types, ranging from medium to fine-grained varieties. In general, the sequence of crystallization of eucrites as deduced from trace element abundances compares favourably with the textural observations of these authors (See Table 43 and the relevant discussion thereon).

In view of the essentially constant major element composition of these samples, absolute enrichment of the trace elements K, Sr, Zr, Y and Ba clearly reflect crystallization from a melt which has been enriched in these elements. The increasing abundance of K, Sr, Zr, Y and Ba through the eucrite sequence is depicted in Figure 18. From this information, the sequence of crystallization appears to be Haraiya - Sioux County - Juvinas - Bereba = Pasamonte - Stannern. The position of Cachari is uncertain. This meteorite is apparently depleted in

figure 18

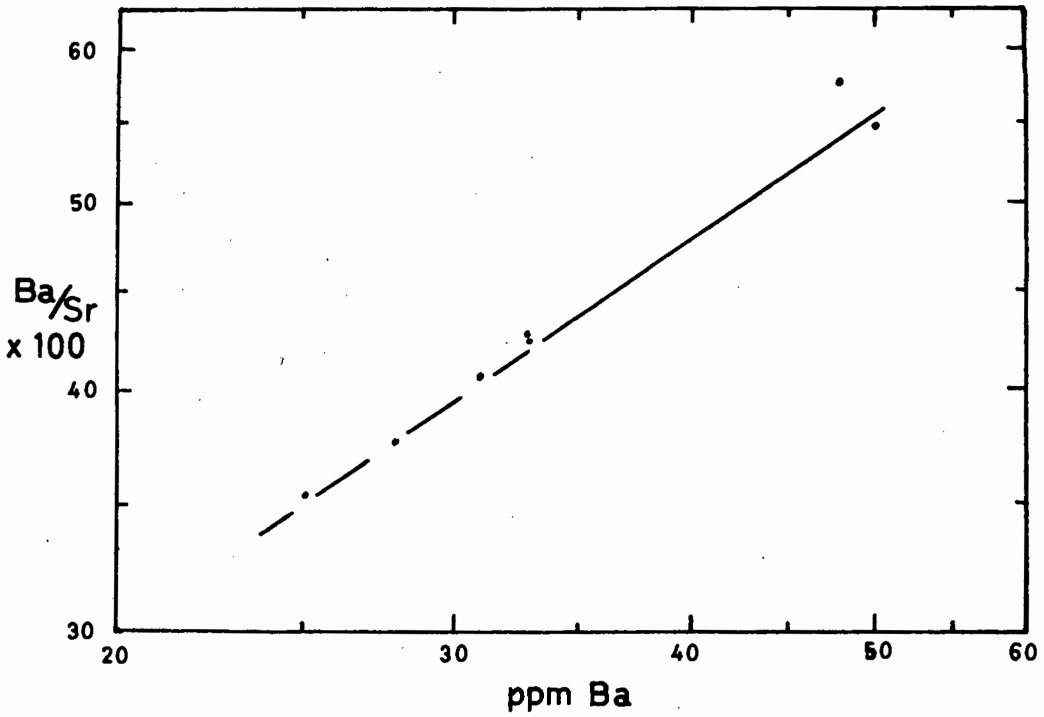


K, Sr, Zr, Y and Ba in eucrites (excluding Binda). The unusual nature of Cachari is evident.

Zr and Y relative to other eucrites (or enriched in K, Sr and Ba). More detailed work on Cachari (the determination of REE in particular) could perhaps throw some light on the reason for its anomalous nature.

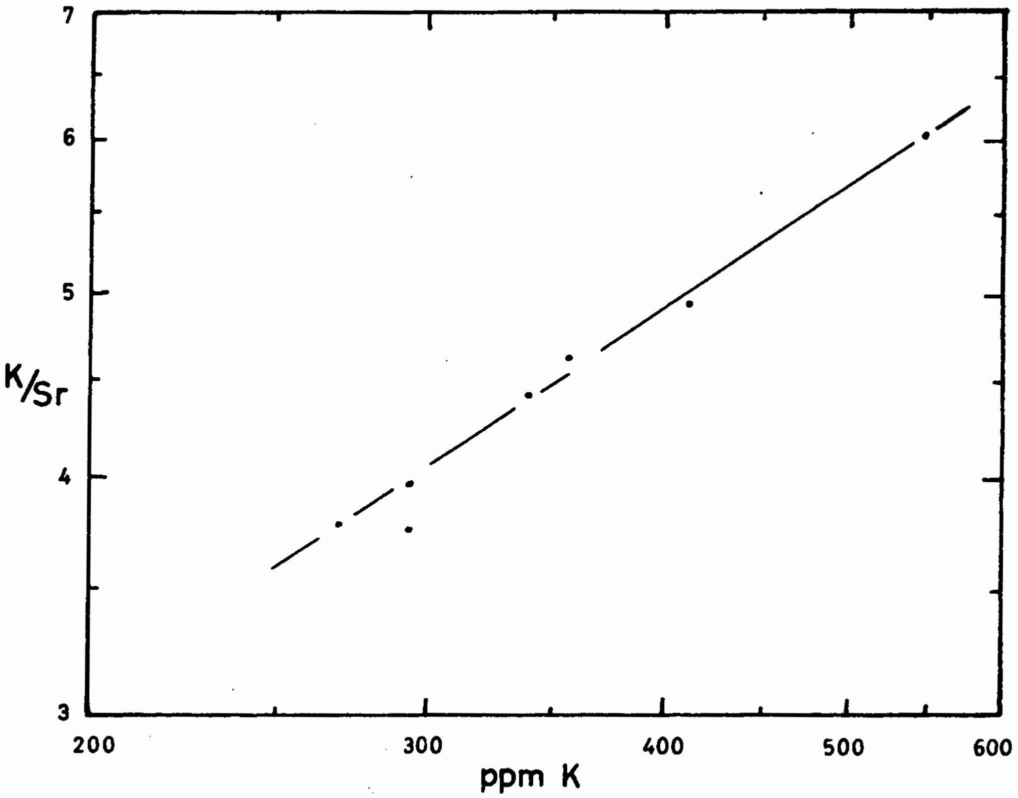
Some interesting features are evident in this sequence. Listed in Table 43 are some inter-element ratios for representatives of this sequence analysed in this work. The order of crystallization is reflected in the increasing Sr/Ca and K/Ca ratios as discussed previously. K and Ba can be seen to enrich faster than Sr in the samples, in accordance with the larger partition coefficient of the latter element in the major K, Ba and Sr bearing phase, plagioclase (Philpotts and Schnetzler 1970b). This faster increase in Ba and K relative to Sr is evident in Figures 9 and 11, where Sr has been plotted against K and Ba respectively. In figure 19, the Ba/Sr ratio is shown plotted against Ba, and in Figure 20, the K/Sr ratio is plotted against K. The change in the Ba/Sr and K/Sr ratios with increasing Ba and K are evident from the deviations of the slopes from unity. It is significant that these relationships are linear over the entire range of differentiation represented by the eucrites studied in this work (Binda excluded), without any tailing off of Sr at Stannern. Because the partition coefficient for Sr in calcic plagioclase is of the order of 1.5 (Philpotts and Schnetzler 1970b), it appears from the trend of increasing Sr that the removal of Sr from the liquid was more than balanced by the simultaneous crystallization of ferro-magnesian minerals with the feldspar (partition coefficient for Sr in clino-pyroxene is of the order of 0.1 or less and for ortho-pyroxene of the order of 0.01 or less so that the effect of these minerals on the liquid is negligible compared to that of plagioclase). The possibility that the partition coefficients in meteorites differ from terrestrial values cannot, of course, be excluded.

figure 19



The relationship between the Ba/Sr ratio and the concentration of Ba in eucrites (Binda excluded).

figure 20



The relationship between the K/Sr ratio and the concentration of K in eucrites (Binda excluded).

TABLE 43

Inter-element ratios in eucrites.

Meteorite.	Sr/Ca	K/Ca	Ba/Sr x100.	K/Ba	K/Sr	Texture.[+]
Haraiya	9.69	36.83	35.2	10.80	3.80	-
Sioux County	9.99	39.81	37.8	10.54	3.99	medium
Juvinas	10.38	45.82	40.3	10.97	4.42	fine
Bereba	10.41	39.25	42.3	8.91	3.77	-
Pasamonte	10.52	48.36	42.9	10.73	4.60	fine
Cachari	11.32	56.07	57.8	8.56	4.95	-
Stannern	11.94	72.05	55.0	10.98	6.03	fine

\+ After Duke and Silver (1967)

The K/Ba ratios listed in Table 43 are also of some interest. No regular change in the K/Ba ratio is observable over the range of composition represented by the eucrites, in spite of the fact that the Ba concentration doubles over this range. If the data of Tera et al (1970) only are used, there does appear to be a slight increase in the K/Ba ratio with increasing K. This may be seen in the data presented in Table 44.

TABLE 44

Inter-element ratios in eucrites.

Meteorite	A			B		
	K	K/Ba	K/Rb	K	K/Ba	K/Rb
Stannern	657	12.4	944	686	11.9	827
Nuevo Laredo	414	10.5	1278	-	-	-
Jonzac	329	11.3	812	300	11.4	909
Pasamonte	327	10.5	1304	-	-	-
Juvinas	322	10.7	1928	298	9.0	903
Sioux County	306	11.2	1490	-	-	-
Bereba	258	9.0	1449	-	-	-
Moore County	159	8.5	3265	193	8.6	2218

A- Data of Tera et al (1970)

B- Data of Schnetzler and Philpotts (1968) and Philpotts and Schnetzler (1970a).

The data of Schnetzler and Philpotts (1968) and Philpotts and Schnetzler (1970a) also reflects a similar trend. It will be noted that the spread of points is rather large, so that the observed trend is by no means perfect. The X-ray fluorescence data for Ba and K presented in this work are probably not sufficiently precise to show such slight relative enrichments.

The regular change in the K/Ba ratio reflects the slightly larger partition coefficient of Ba in plagioclase feldspar (Philpotts and Schnetzler 1970b), resulting in a faster enrichment of K in the liquid. This is a situation similar to that observed for Ba and Sr and K and Sr.

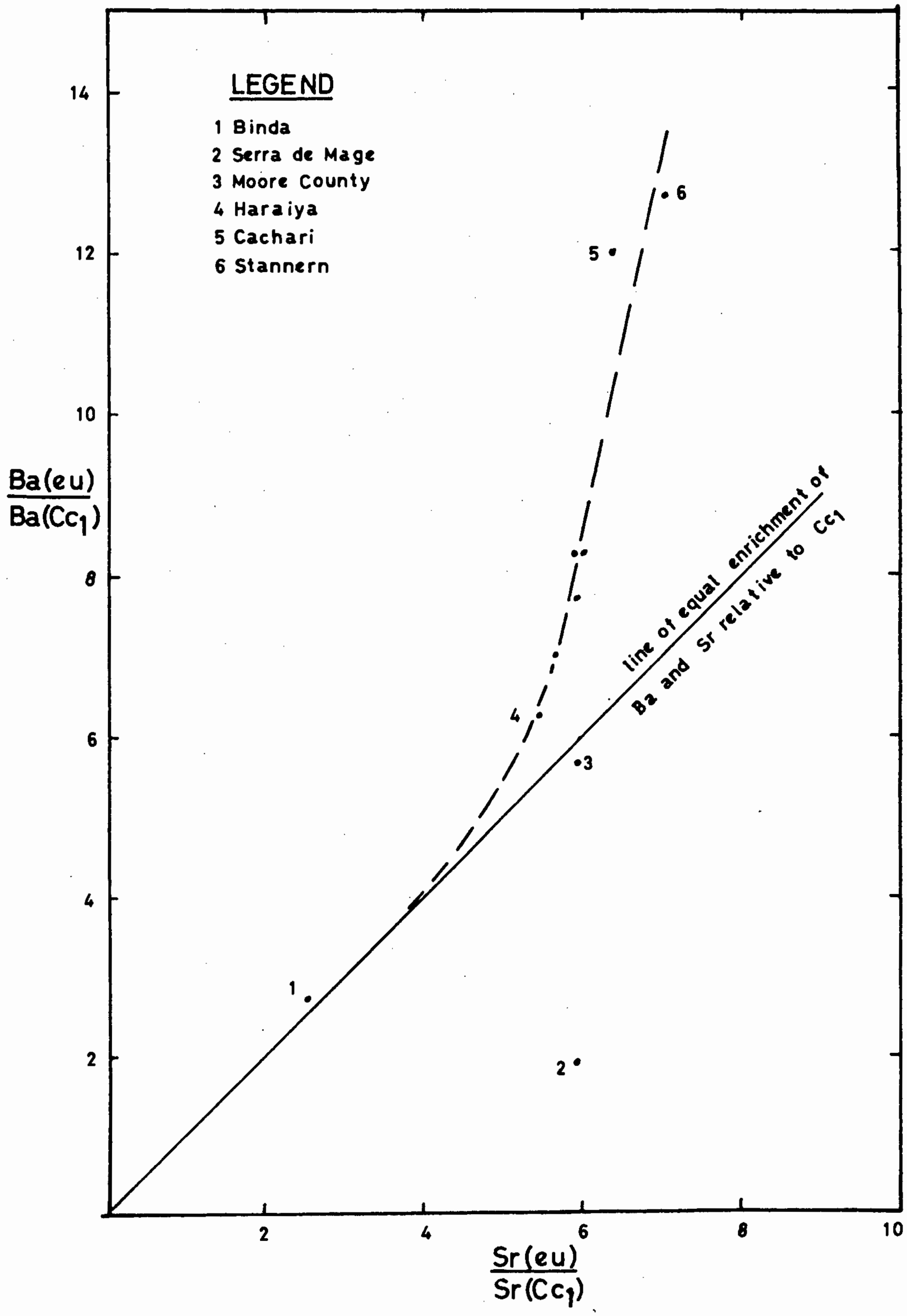
The K/Rb ratios of eucrites are particularly interesting. Using only the data of Tera et al (1970), it is clear that no regular relationship exists between the K/Rb ratio and the absolute K abundance. Such a relationship might have been expected from consideration of the partition coefficients for K and Rb in plagioclase (the major carrier of Rb and K in these meteorites) as given by Philpotts and Schnetzler (1970b). This rather unusual behavior does not seem to be due to analytical problems, as replicate analyses presented by Tera et al (1970) agree well in most instances. It is conceivable that small amounts of liquid trapped during the crystallization of these meteorites could be responsible for these anomalous ratios. The effect of such trapped liquid will differ from element to element, depending on the partition coefficient of that element in the phases forming the meteorite. For example, the Juvinas plagioclase analysed by Schnetzler and Philpotts (1969) and Philpotts and Schnetzler (1970a) coexisted with a liquid containing 5580 ppm K, 548 ppm Ba and 10.8 ppm Rb, assuming that the mineral/matrix partition coefficients were 0.131, 0.132 and 0.0390 for K, Ba and Rb respectively. If 1 % of this liquid were trapped in a meteorite similar to Juvinas, which contained 50 %

pyroxene (assumed to have the composition of Juvinas pyroxene) the contribution of this trapped material to the bulk K, Ba and Rb would be 14 %, 14% and 29 % respectively. The lower the partition coefficient, the greater the effect of the trapped liquid. Thus, small quantities of trapped liquid could be responsible for marked changes in the K/Rb ratio, while the K/Ba ratio remains essentially unaffected. On this basis, one might expect some scatter in the K/Sr relationship, but this does not appear to be the case (Figure 20). The alternative explanation for the lack of correlation between K/Rb ratio and absoulte K content is selective volatilization of Rb relative to K after the formation of these meteorites. Careful microprobe examination of eucrites should be undertaken with a view to establishing which alternative is, in fact, responsible.

(ii) The crystallization history of diogenites and eucrites: It is of interest to consider the implications of the trace element abundances determined in this work on the parent material of diogenites and eucrites.

In Figure 21, the data for Ba and Sr obtained in this work has been normalized to the carbonaceous chondrite (Cc_1) Ba and Sr abundances of Tera et al (1970) (4 and 13 ppm respectively), and the normalized values have been plotted against one another. The trend of increasing Ba relative to Sr in eucrites, which was discussed earlier, is evident in this figure. The curve defined by the normalized Ba and Sr abundances in eucrites (including Binda) appears to be indistinguishable from the line of equal enrichment of Ba and Sr from a normalized Ba value of about 4 downwards. This could be fortuitous, or it could indicate that the parent liquid from which the eucrites crystallized had relative Ba and Sr abundances similar to Cc_1 chondrites. The crystallization of phases such as hypersthene and olivine from such a liquid are not likely to produce relative changes in Ba and Sr abundances, as the partition coefficients for these elements in these minerals are small.

figure 21



The degree of enrichment of Ba and Sr in eucrites relative to Cc_1 chondrites.

Thus, only absolute enrichments are likely to occur. In rocks representing these early-formed crystalline phases, the Ba and Sr abundances are likely to be dominated by intercumulus phases (trapped liquid) and will reflect the Ba/Sr ratio of the original parent liquid. With the appearance of plagioclase on the liquidus, the situation changes rapidly. Both Ba and Sr substitute in plagioclase, the latter exceeding the former. Thus, as the crystallization of plagioclase proceeds, the relative enrichments of Ba and Sr in the crystalline phases change, in response to the changes brought about in the liquid. Binda lies very close to the line of equal enrichment of Sr and Ba (Figure 21) in spite of the presence of 25 (modal) % plagioclase (Duke and Silver 1967). The Ba and Sr abundances in this meteorite are thus possibly dominated by intercumulus plagioclase (see also the remarks above on the crystallization order). It is clear from its normalized Ba and Sr abundances that little plagioclase crystallization could have occurred prior to the crystallization of Binda (if the initial Ba/Sr ratio of the liquid was chondritic), and, in fact, Figure 21 shows that the start of the marked enrichment of Ba relative to Sr, the result of plagioclase crystallization, occurred prior to the time of formation of Haraiya, but subsequent to the formation of Binda.

Serra de Mage occupies a unique position in Figure 21. This accords with the suggestion of Schnetzler and Philpotts (1968) that it is a plagioclase cumulate, as pure or almost pure plagioclase forming from a melt is likely to contain Sr in excess of that in the liquid, but less Ba than the liquid, according to the partition coefficients of Philpotts and Schnetzler (1970b). The point of origin of Serra de Mage relative to other eucrites was considered to be prior to or shortly after Binda. The latter posibility is more probable. It is clear that its crystallization did not have a very marked effect on the liquid composition. Extensive plagioclase fractionation would most certainly have produced strong enrichments of Ba relative to Sr in the liquid phase. A similar argument could be applied using the REE, as Serra de Mage has a marked positive Eu anomaly (Schnetzler and Philpotts 1968), while later crystallizing phases show no marked Eu anomaly. Moore County also occupies a position in the field of plagioclase cumulates, but close to the line of equal enrichment of Ba and Sr. Schnetzler and Philpotts (1968) have suggested that this meteorite represents a plagioclase - pyroxene cumulate which has undergone some closed - system competition for trace elements between the major minerals. The fact that this meteorite lies close to the line of equal enrichment might reflect the presence of fairly large quantities of trapped liquid which made the postulated closed - system competition possible and partly nullified the effect of the accumulated plagioclase on its relative Ba and Sr abundances. The crystallization of Moore County (and possibly Serra de Mage) may explain the fact that Haraiya, an early - formed eucrite, crystallized from a liquid in which the relative Ba and Sr abundances had been altered slightly since its generation.

It is possible to extrapolate back to the original composition of the original parent material of eucrites and diogenites from consideration of Ba abundances, or at least place restrictions on the abundances of certain elements within this material. In order to do this, it is necessary to know the concentration of the elements concerned in a particular mineral, as well as their partition coefficients for that mineral. Fortunately, Schnetzler and Philpotts (1968) and Philpotts and Schnetzler (1970a) have analysed mineral phases which provide a useful means of ascertaining the nature of the eucrite parent liquid. If one assumes a partition coefficient (mineral/matrix) for K and Ba in plagioclase of 0.13 and 0.15 respectively, not an unreasonable assumption in terms of the partition coefficients presented by Philpotts and Schnetzler (1970b), this implies that Juvinas plagioclase (72.4 ppm Ba and 731 ppm K) must have crystallized from a liquid containing 483 ppm Ba and 5580 ppm K. The Ba in this liquid is enriched 122 times relative to carbonaceous chondrites (Cc_1 assumed to contain 4 ppm Ba - Tera et al 1970), or 95 times relative to HL chondrites (5ppm, this work).

Clearly, it is unlikely for such a liquid to have been produced from an initial melt containing Ba at chondritic abundance levels. If the initial liquid did have Cc_1 Ba abundance, this implies that the material crystallizing at the time of Juvinas represents the last 1 % (or less) of the original melt. It seems most unusual that this last 1 % of crystallized liquid is so widely represented in the howardites. One might expect a greater proportion of diogenite - rich howardites (if any howardites at all) if the original liquid had been chondritic. More likely, the parent material was enriched in Ba relative to chondrites. This conclusion is based on the assumed partition coefficients, the purity of the separated phases of the meteorite concerned and on the analytical accuracy. It would be gratifying if the liquid composition could be confirmed by applying partition coefficients to the pyroxene. The pigeonite partition coefficients presented by Philpotts and Schnetzler (1970b) are so small (0.00344 for K and 0.00041 for Ba) that if these are applicable then the measured K and Ba in the pyroxene of Juvinas can only be due to feldspar impurity. Because of the range of partition coefficients available for pyroxene in general, it is not possible to use the analysed pyroxene separate from Juvinas (Schnetzler and Philpotts 1968) as a cross check. In the absence of of more analyses of separated phases, and an improved knowledge of the partition coefficients concerned, it is not possible to argue further along these lines concerning the non-chondritic nature of the eucrite-diogenite parent liquid. One point is, however, quite clear. The liquid from which Juvinas crystallized was enriched approximately 6 times in K relative to Cc_1 chondrites, while Ba was enriched roughly 120 times relative to the Cc_1 group. As the partition coefficients for K and Ba are similar, it is quite clear that either the parent liquid from which the eucrites and diogenites formed was enriched in Ba relative to Cc_1 chondrites, depleted in K relative to these meteorites, or both.

Certain restrictions can also be placed on the bulk composition of the parent liquid from which diogenites and eucrites formed based on the observations made in this work. It will be recalled that of the diogenites studied in this work, the first to have crystallized was considered to be Tatahouine or possibly Shalka. Neither meteorite contains olivine while a later-formed meteorite does (Ellemeet - Mason 1963a). The implication is that crystallization began in the pyroxene field of the system Anorthite-Quartz-Forsterite (see Mason 1962, page 117), and not in the olivine field as suggested by Mason. Thus, the first formed material consisted entirely of pyroxene. As crystallization proceded, the liquid phase intersected the olivine-pyroxene cotectic, and some olivine began to crystallize along with pyroxene forming diogenites similar to Ellemeet and Roda. Further, the low Ni content of these early-formed phases indicates the absence of appreciable quantities of metal phase. Either separation of the metal was near perfect, or the parent material contained no metal phase. Representatives of later events are few in number. This may reflect poor sampling by the earth, or it could be the result of the mixing process which formed the howardites, wherein the intermediate representatives were destroyed. Some olivine and plagioclase cumulates probably formed, although few representatives of these are known. The final stages are well represented by the eucrites, which could represent, in the main, crystallization at the eutectic in the system Anorthite-Quartz-Forsterite.

The relative abundances of diogenites and eucrites are of some interest. According to Keil (1969a), 7 diogenites (Johnstown excluded) and 22 eucrites are known (excluding Macibini - see above, Medanitos - abnormal composition, Symes and Hutchinson 1970, Moore County and Serra de Mage, Shergotty, Padvarninkai and Zagami - Shergottites, Mason 1967). Binda, Serra de Mage and Moore County may be regarded as a separate but related class along with Chassigny as another possible representative. If the abundances reflect the actual proportions of the daughter products produced by the differentiation process, it is clear that the original parent was not chondritic, but was enriched in all refractory elements relative to common chondrites. Such a weighted average has been calculated from the data of this work, and is listed together with average chondrite compositions in Table 45. Little reliance can be placed on the trace element content (including K) of such an average, due to variability

TABLE 45

Weighted average composition for diogenites-eucrites.[+]

	Weighted average	HL(ave)	L(ave)	H(ave)
Fe %	14.1	23.6	21.5	27.0
Mn %	0.43	0.15	0.26	0.23
Ti %	0.33	0.09	0.06	0.06
Ca %	5.76	1.8	1.3	1.2
Cr %	0.41	0.35	0.35	0.35
P %	0.03	0.1	0.1	0.1
Si %	23.3	15.6	18.55	16.7
Al %	5.2	1.7	1.2	1.1
Mg %	7.2	14.7	14.9	13.9
Na %	0.31	0.31	0.69	0.65
K ppm	280	288	850	780
Sr "	59	14	11	9
Zr "	41	2	9	8
Y "	17	2	2	2
Ba "	27	5	3.7	3.2

[+] Data from: Wiik (1970), von Michaelis et al (1969b), Schmitt et al (1967), Reed et al (1960) and this work.

of these elements in eucrites. However, the enrichment in Ca, Al and Ti in this weighted average relative to chondrites is clear. Whether this has any significance depends on whether the meteorite population has been sampled randomly or not. This is impossible to determine.

However, the discussion of the distribution of Ba lends strength to the observation that the parent magma from which diogenites and eucrites crystallized was, in fact, enriched in refractory elements relative to the chondrites. Similar conclusions have been reached for the earth (Gast 1968) and the moon (Gast and Hubbard 1970).

7. Conclusion.

From the foregoing discussion, it would appear that the origin of howardites, diogenites and eucrites was by no means simple. Some evidence exists which suggests that the original parent liquid from which these meteorites formed was not chondritic, but was enriched in refractory elements relative to chondrites. The suggestion of a non-chondritic parent material is in accordance with the observations of Taylor et al (1965) based on oxygen isotopes, i.e. howardites, eucrites and diogenites are poorer in O^{18} than chondrites, contrary to what would be expected if these meteorites had been derived from a chondritic parent. Further, it was pointed out in the above discussion that the parent liquid from which the diogenites and eucrites formed was apparently depleted in heavy alkali metals relative to chondrites (in agreement with the conclusions of Gast 1960), enriched in refractory elements and apparently contained no metal phase. Material of this composition could have formed in a nebula if the high temperature compounds postulated by Larimer (1967), which condensed early, were isolated before appreciable metal condensation occurred (temperatures higher than 1300°K - Larimer and Anders 1967). A high temperature material enriched in refractory elements has been recognized as discrete inclusions in HL chondrites. Kurat (1970) observed discrete phases in Lancé which showed strong enrichments of Y, Zr, Ti, Al and Ca relative to chondrites. Similar Ca-Al rich phases have been observed in Allende by Marvin et al (1970) and by Clarke et al (1971), and have apparently also been observed in Vigărano , Kaba and Bali (Clarke et al 1971). Keil et al (1968) have identified similar material in Leoville, but consider it to be achondritic.

After the differentiation process was complete, and the eucrites had solidified, collisions broke up the differentiated material, and mixed them to form the howardites. The impacting material may have been chondritic (Jérome and Goles, 1970). It was probably at this stage that metal and silicate mixed to form the mesosiderites, as has been suggested by Powell (1971). In terms of the model proposed here, the metal itself is not directly related to the genesis of eucrites and diogenites, but could have represented a surface coating on the achondrite parent body. McCarthy and Ahrens (1971) have shown that the silicate portion of mesosiderites does not, however, appear to be normal howarditic material as implied by Powell (1971). However, this must be confirmed by additional analyses of mesosiderites.

During the break up of the parent body, some representatives of the differentiation sequence could quite conceivably have been lost, with the result that a somewhat biased distribution of samples has been captured by the earth.

Although the processes which were responsiblefor the formation of howardites, eucrites and diogenites have been discussed in some detail, no consideration will be given to the site where such processes occured (i.e. moon, asteroids etc.), as this is beyond the scope of this work.

ENSTATITE ACHONDRITES

The unique character of the enstatite achondrites was first recognized by Prior, who separated them from the diogenites and elevated them to a class on their own. Mason (1962) pointed out that these meteorites bear a closer resemblance to the enstatite chondrites than to any achondrite class. This has been confirmed by oxygen isotope studies by Taylor et al (1965), who found that the enstatite achondrites were similar to chondrites, and distinctly different from most other achondrite types. The mineralogy of the silicate fraction of both enstatite achondrites and chondrites is similar, both consisting essentially of Fe poor enstatite and some olivine (Ringwood 1961, Reid and Cohen 1967, Mason 1962). The enstatite chondrites differ in that they contain appreciable quantities of Ni-Fe metal, while this phase is virtually absent from the enstatite achondrites (except Shallowater - Mason 1962). Another remarkable similarity between the enstatite chondrites and achondrites is their marked degree of reduction, quite unlike that of any other meteorite type (Reid and Cohen, 1967, Keil and Fredriksson 1963).

Ringwood (1961) and Mason (1962) suggested that enstatite achondrites could represent the silicate portion of enstatite chondrite - like material which had melted, and from which the metal phase had been separated by gravity settling. A similar suggestion was made by Keil and Fredriksson (1963).

Recently, the enstatite achondrites have been subjected to detailed mineralogical studies, which have shown that a simple model of separation of metal from an enstatite chondrite to produce an enstatite achondrite is untenable. Thus, Keil (1969b), from his observations on the Ti content of troilite, concluded that enstatite achondrites are not equivalent to the non-metallic fraction of enstatite chondrites. Wasson and Wai (1970) made extremely pertinent observations regarding the association of enstatite chondrites and achondrites. They found that the gradation in properties of enstatite chondrites observed by Mason (1966) and Keil (1969b) (e.g. Si and Ni in kamacite, schreibersite composition, degree of crystallization) appear to extend into the achondrites, and they concluded from this that the same processes which formed the enstatite chondrites were probably responsible for the formation of the enstatite achondrites as well.

It is clear that if the origin of the enstatite achondrites is to be understood, their chemistry must be seen in the light of that of the enstatite chondrites.

1. Inter-element relationships in enstatite chondrites and achondrites.

Three enstatite achondrites were available for study in this work - Cumberland Falls, Norton County and Shallowater. The analyses of enstatite chondrites of von Michaelis et al (1969b) have been used for comparative purposes. These analyses were carried out using the same technique and X-ray spectrometer as employed in this work. In addition to these, one analysis of an enstatite achondrite has been taken from the literature.

(a) **Fe - Si and Mg - Fe relationships:** Mason (1966) and Keil (1968) observed that the average Fe content of Type II enstatite chondrites was lower than that of Type I. Wasson and Wai (1970) noticed that this trend, as indicated by the Fe/Si ratio, extended to the enstatite achondrites as well. This relationship is best indicated in another form, however, viz. as a plot of weight per cent Fe against weight per cent Si. Such a plot is shown in Figure 22. The inverse trend is clear. A distinct flattening off of the fitted curve is evident at higher Fe abundances. Linearity over the whole range can be improved if the Si dissolved in the metal phase is subtracted from the total Si as is indicated in Figure 22 by crosses. The contribution of the Si dissolved in

figure 22

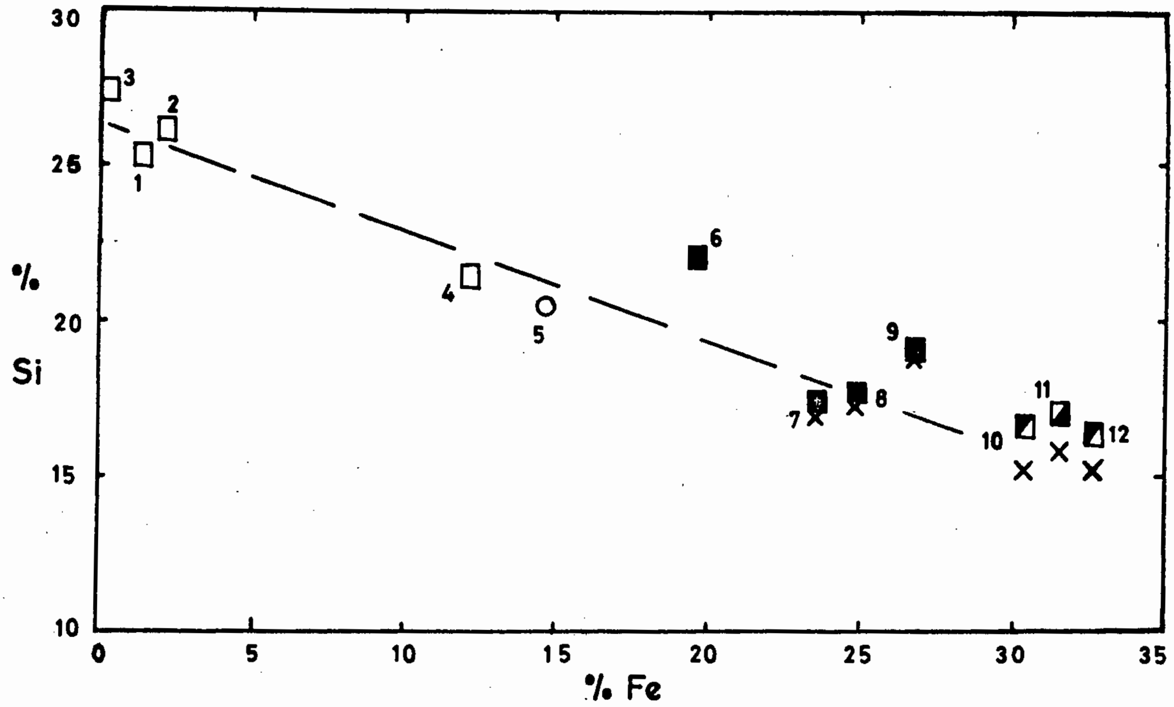
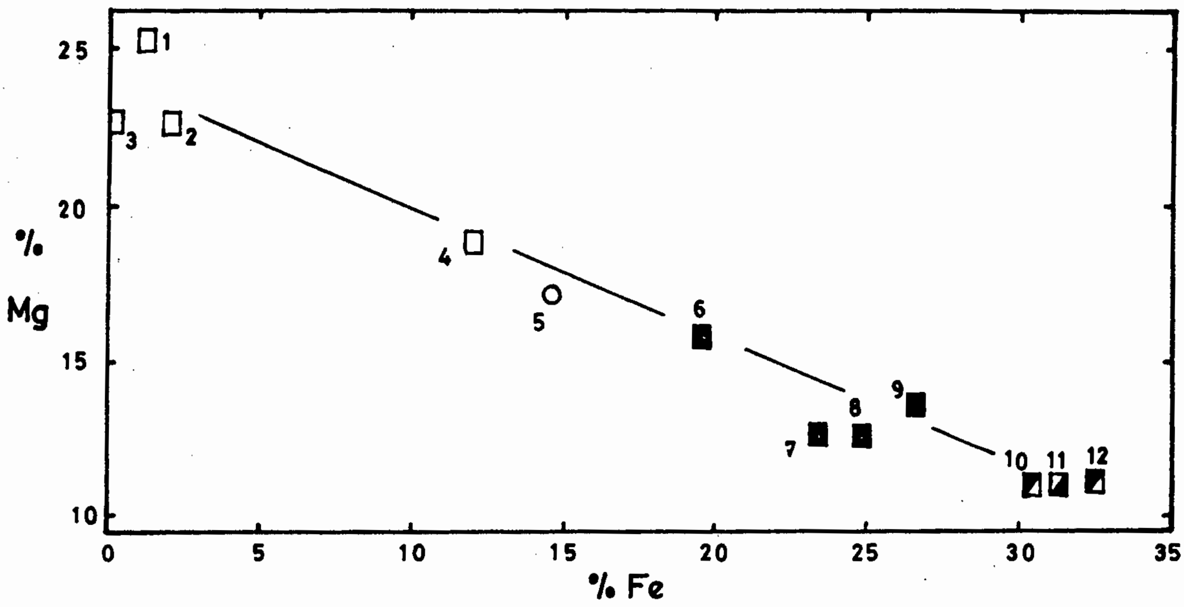


figure 23



LEGEND TO FIGURES 22 and 23

☐ ENSTATITE ACHONDRITES
ENSTATITE CHONDRITES
◩ TYPE I
◪ INTERMEDIATE
■ TYPE II
○ CHONDRITE INCLUSION IN CUMBERLAND FALLS

1 Norton County
2 Cumberland Falls
3 Khor Temiki
4 Shallowater
5 Cumberland Falls chondrite
6 Blithfield
7 Hvittis
8 Atlanta
9 Pillistfer
10 Indarch
11 St. Marks
12 Abee

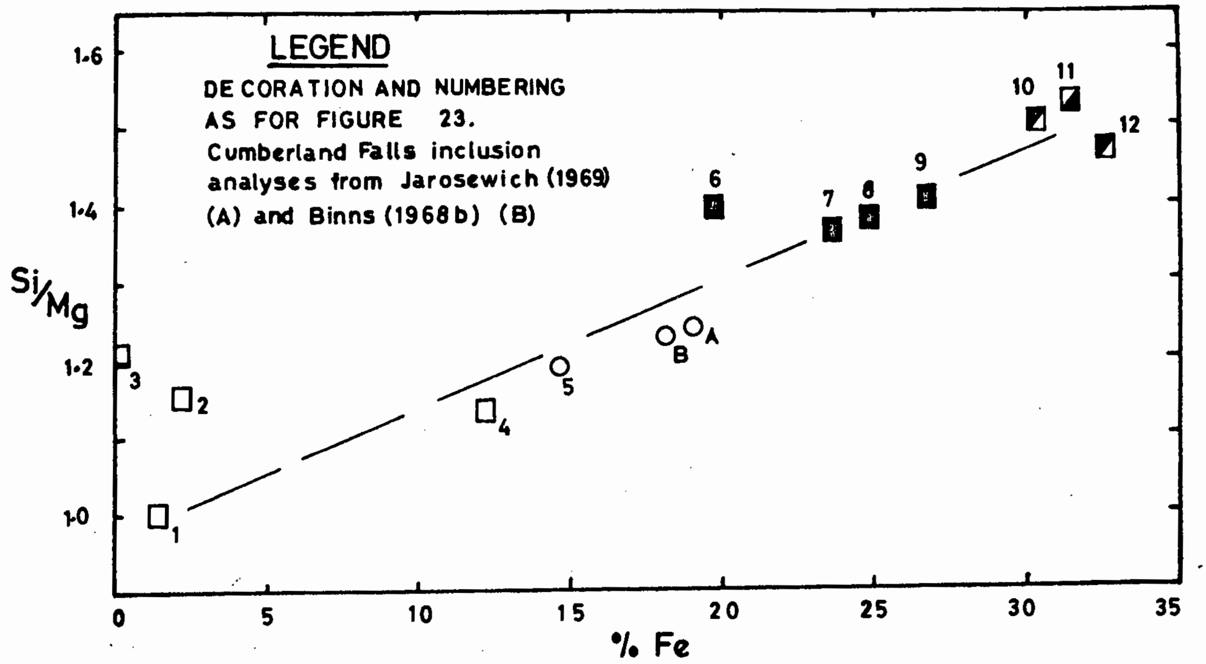
The relationship between Fe and Si and Mg in enstatite chondrites and achondrites.

kamacite was estimated using the kamacite analyses and metal abundances (wet chemical) of Keil (1968). A plot of Mg against Fe also produces a good negative correlation, apparently linear over the whole composition range(Fig 23). The chondrite Blithfield is anomalous. Negative correlations observed in Figures 22 and 23 are not wholly unexpected, and arise from the dilution of essentially pure enstatite by metal. It is nevertheless of some significance that achondrites and chondrites lie on the same line in these figures. Had there been significant quantities of lithophile elements other than Mg and Si present in either enstatite achondrites or chondrites, then both types would obviously not have defined the same trend line.

A more significant feature of these relationships, however, is the fact that the slopes of the Fe-Si and Mg-Fe trends differ. This is discussed at length in the next section.

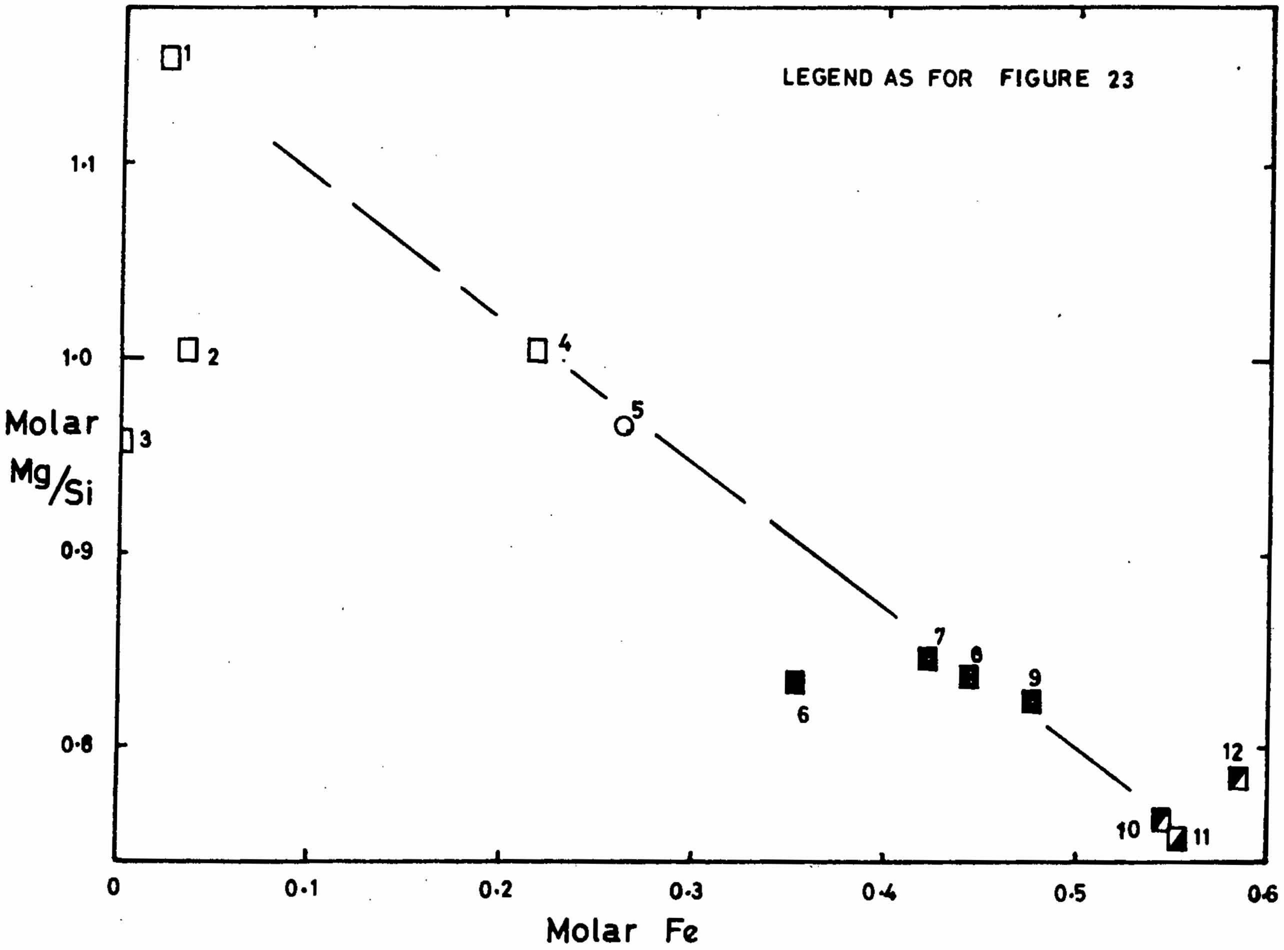
(b) The Si/Mg ratio: Keil (1968) has drawn attention to the fact that the Si/Mg ratio is slightly fractionated between Type I and Type II enstatite chondrites. Wasson and Wai (1970) observed that the ratio Mg/Si increased in the sequence Type I, Type II enstate chondrites, enstatite achondrites. This relationship has been re-examined in this work using more modern data where possible. Shown if Figure 24 is a plot of Si/Mg ratio against Fe. The trend of decreasing Si/Mg ratio with decreasing Fe observed in the enstatite chondrites seems to include some achondrites as well - viz. Shallowater and Norton County. The remaining achondrites for which analyses are available have a significantly higher Si/Mg ratio than Norton County and a significantly lower Fe content than Shallowater. The possibility that the change in the Si/Mg ratio was brought about by the presence of Si in the metal phase was investigated using the data of Keil (1968) and of this work. It was found that the change in the Si/Mg ratio was too large to be markedly affected by removing the Si dissolved in the kamacite. Other factors

figure 24



The relationship between the Si/Mg ratio and the abundance of Fe in enstatite chondrites and achondrites.

figure 25



The data shown in figure 24 replotted on a molar basis.

must be responsible.

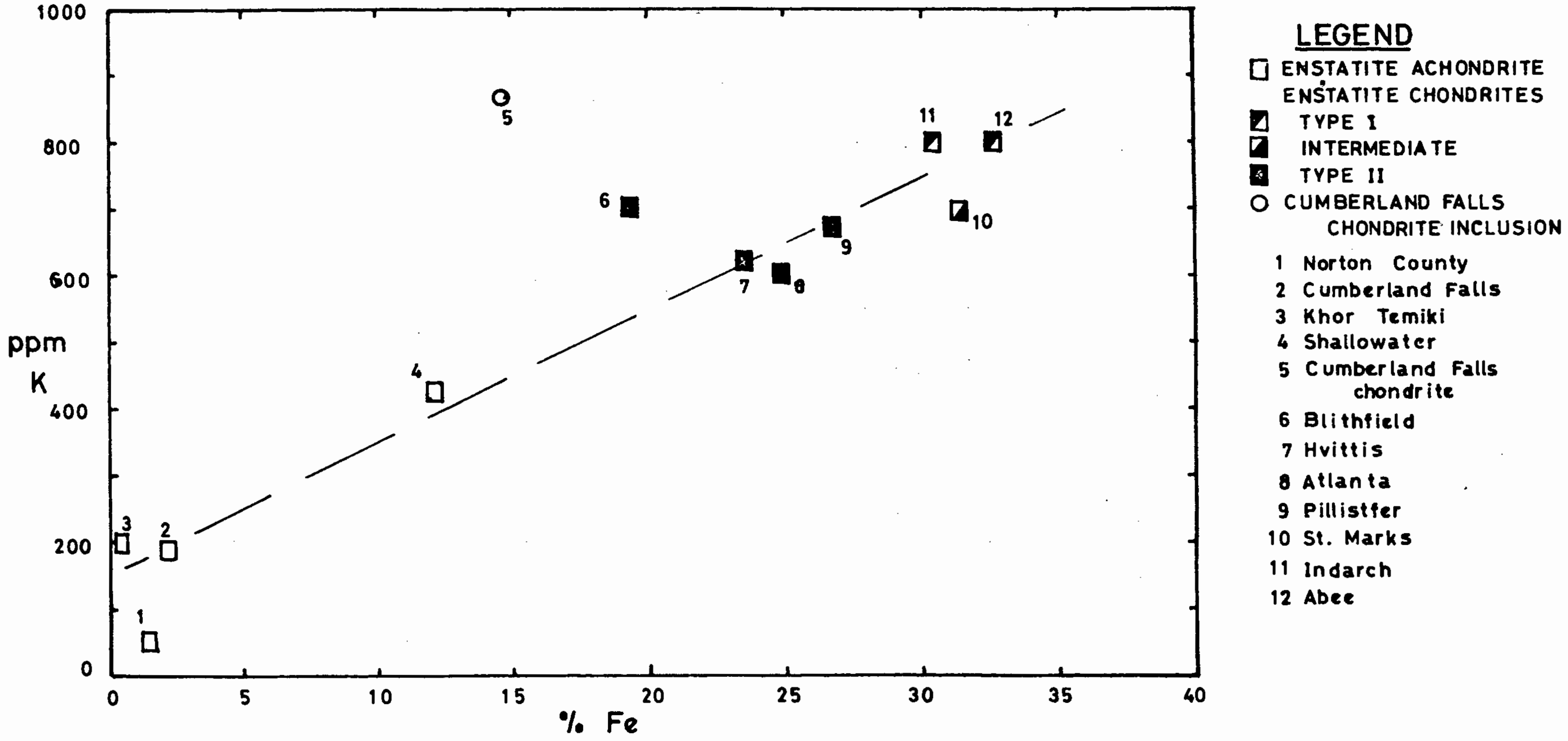
The data used to construct Figure 24 has been replotted on a molar basis in Figure 25. A molar Mg/Si ratio greater than 1.0 implies Mg in excess over that required to form enstatite, resulting in the presence of olivine, assuming an equilibrium mineral assemblage. A Mg/Si ratio of less than 1.0 indicates that olivine will not occur if the assemblage is in equilibrium. Binns (1967b) has described olivine in Type I enstatite chondrites occuring adjacent to free quartz, clearly indicating the non-equilibrium nature of the mineral assemblage in these meteorites. Norton County is the only enstatite meteorite studied which has a molar Si/Mg ratio significantly in excess of 1.0.

(c) The Fe-K relationship: Using the data of von Michaelis et al (1969b), Hey and Easton (1967) and of this work, it appears that K and Fe in enstatite achondrites and chondrites are positively correlated with one another (Figure 26). In this relationship, as in those discussed previously, Blithfield is anomalous. Norton County appears to differ slightly from other enstatite achondrites, as does Shallowater. The significance of this important relationship is discussed in a later section.

2. The chondritic inclusion in the Cumberland Falls achondrite.

A 0.69 g fragment of the black chondritic fragment from the Cumberland Falls meteorite was analysed, in addition to the achondritic fraction. This included material has recently been described by Binns (1968b) who presented an analysis by A.J.Easton. In addition, Jarosewich (1967) has analysed a chondritic fragment from Cumberland Falls as well. The three analyses are presented in Table 46 to facilitate comparison.

figure 26



The relationship between Fe and K in enstatite chondrites and achondrites.

TABLE 46

Analyses of the chondrite inclusion in the Cumberland Falls achondrite.[+]

	A.J.Easton	E.Jarosewich	This work
Fe	17.9	19.00	14.70
MnO	0.50	0.66	0.39
TiO_2	0.11	0.20	0.11
CaO	1.64	2.21	2.00
Cr_2O_3	0.39	0.53	0.67
SiO_2	42.48	41.77	44.26
Al_2O_3	3.04	2.13	1.95
MgO	26.75	26.08	28.73
Na_2O	1.20	1.31	nd
K_2O	0.08	0.08	0.11

[+] Data expressed as weight %

There appear to be some slight but nevertheless significant differences between the analysis presented in this work and those of Jarosewich and Easton. The Fe measured in this work is lower than that obtained by the other analysts, while Si and Mg are higher. This could be due to the fact that the small sample analysed in this work was not representative (i.e. lower metal), although the Si/Mg ratio calculated from the analysis presented here (1.18) is slightly lower than those of Easton (1.23) and Jarosewich (1.24). Further, the Al_2O_3 content obtained for the inclusion in this study is lower than both Easton's and Jarosewich's values, suggesting that the differences in composition of the different samples analysed are real and not simply due to non-representative sampling.

Binns (1968b) has suggested that the chondrite inclusion in Cumberland Falls is intermediate in character between L group chondrites and enstatite chondrites. The chondrite fragment analysed in this work, however, shows certain characteristics which place it in an intermediate position between enstatite chondrites and achondrites (see figures 22 - 25). The fragments analysed by Jarosewich and Easton show a similar tendency (Figure 24), although they also show close affinities with the L group chondrites - more so than the fragment analysed in this work. In his examination of the mineral chemistry of this chondrite fragment, Binns found that the ferromagnesian minerals were almost free of iron, but significantly the metal contained no Si. If this meteorite is, in fact, intermediate between enstatite chondrites and achondrites, one might expect the kamacite to contain at least 1.0 % Si. Its absence may reflect oxidation and removal of Si from the metal prior to its being included in the brecciated Cumberland Falls achondrite, although this does seem to be in conflict with Binns' conclusion that the meteorite is unequilibrated. Unfortunately, the K content cannot be used to resolve the dilemma, as the value obtained in this work is most probably too high - perhaps the result of excessive handling of the small fragment prior to analysis. Assuming this chondrite to be intermediate between chondrites and achondrites, one might expect it to contain about 500 ppm K, a value quite close to that obtained by Easton and Jarosewich.

3. Some implications of the inter-element relationships among enstatite chondrites and achondrites.

The evolutionary sequence observed amongst the enstatite achondrites themselves by Wasson and Wai (1970) is not evident in the data of this work. Shallowater and Norton County differ in some respects from other enstatite achondrites, and always appear to represent a continuation of the chemical trends evident in the Types I and II enstatite chondrites. Similarly, in terms of its bulk composition, the chondrite inclusion from the Cumberland Falls meteorite also belongs to this sequence. These trends have some bearing on the origin of enstatite achondrites.

The regular change in the Si/Mg ratio with increase in the metal content is not the type likely to be produced by igneous differentiation of an enstatite chondrite. Removal of metal obviously will not affect the Si/Mg ratio, unless the removed metal contains an appreciable (and constant) amount of Si. The small quantity of metal remaining in these meteorites contains variable Si (Wasson and Wai 1970), which is apparently related to the absolute Fe content, suggesting that removal of an Si rich metal phase was not responsible for Si/Mg fractionation. Simultaneous crystallization of a silicate phase with the metal could cause fractionation of the Si/Mg ratio. In order to decrease the Si/Mg ratio of a liquid of Type I composition however, enstatite would have to crystallize and be removed. Such a model is self-defeating.

The Fe - K relationship observed in the enstatite meteorites is difficult to explain in terms of simple igneous differentiation, as this would be expected to produce the reverse trend. Selective volatization could be invoked to explain the inverse trend observed, although special conditions of formation would have to be postulated to explain the correlation between the extent of volatilization of K and the Fe abundance.

In addition to the above objections to an igneous differentiation origin for enstatite achondrites, those of Keil (1969b) should be added as well. He observed that the Ti content of troilite in enstatite achondrites was considerably greater than that of the chondrites, in spite of the similar bulk Ti contents. Thus, in the postulated differentiation, mass balance requires that all Ti be concentrated in the melt, while most of the sulphide and metal be removed, a process he concluded to be highly improbable. The conclusion of Wasson and Wai (1970) that igneous differentiation was not responsible for the formation of enstatite achondrites is supported by the data presented in this work.

As mentioned above, Norton County and Shallowater appear to differ from other enstatite achondrites in some respects. The unique character of Shallowater is well known (Mason 1962, Wasson and Wai 1970) and will not be discussed here. Norton County differs from other enstatite achondrites in that its Si/Mg ratio is significantly lower than that of the other representatives of this group of meteorites. In addition, its K content seems to be somewhat lower. In terms of the parameters investigated by Wasson and Wai, however, (schreibersite, perryite and metal composition, Mn/Si and Na/Si ratios) this meteorite does not appear to be abnormal. It seems therefore that the observed differences do not indicate any fundamentally different processes operative in the formation of Norton County. The suggestion of Wasson and Wai (1970) that Norton County represents a point in the evolutionary sequence immediately prior to Shallowater and subsequent to the remaining enstatite achondrites seems to be supported by this observation.

4. Boundary conditions for the formation of the enstatite chondrites and achondrites.

The igneous differentiation model for the origin of enstatite achondrites proposed by Ringwood (1961), Mason (1962) and Keil and Fredriksson (1963), amongst others, does not provide a satisfactory explanation of the observed chemical features of these meteorites. Rather, they appear to have been formed together with the enstatite chondrites by some dynamic process or processes. The inter-element relationships discussed in the previous section place some restrictions on models for the origin of these meteorites. The most important restrictions are:-

(i) The presence of Si in the metal. Such Si must have been present in the metal prior to accretion of the enstatite meteorites, as the metal in Type I enstatite chondrites is richest in Si, yet their silicate assemblage is in disequilibrium, indicating that post-

accretion reduction was minimal (Keil 1969b, Binns 1967).
(ii) Ti distribution. Some Ti has been observed in the silicate phase of Type I enstatite chondrites (Easton and Hey 1968), indicating that it must have been present as such in the silicate prior to accretion. This is apparently anomalous, as the Type II enstatite chondrites and enstatite achondrites show only chalcophilic Ti, in spite of the lower Si content of their kamacite (Keil 1968, Wasson and Wai 1970).
(iii) The varying proportion of metal phase.
(iv) The decrease in the Si/Mg ratio with increase in the proportion of silicate.
(v) The changes in mineral composition (Ti in troilite and daubreelite, Si and Ni in schreibersite) through the enstatite sequence.
(vi) The positive correlation between kamacite content and alkali metals.
In addition to these, cosmic ray exposure ages and noble gas contents place further restrictions on any model for the origin of these meteorites.

The igneous differentiation model has already been discussed. An alternative model proposed by Wasson and Wai (1970) will now be considered in terms of the above restrictions. In this model, the authors assume complete condensation prior to the accretion of the enstatite-rich meteorites. This is difficult to reconcile with the observed behavior of Si in kamacite and Ti distribution. According to Keil (1968) the range of Si in different kamacite grains in Type I enstatite chondrites is relatively small, and the Si content is high (3.2%), indicating high and uniform state of reduction in the unaccreted dust. However, Ti occurs in the silicate in small quantities associated with oxygen (see (ii) above), a feature in marked contrast to the high and uniformly reduced state of the unaccreted dust. (Ti is chalcophile even when only minute traces of Si are present in the metal). Wasson and Wai explain the varying proportion of metal by the superior adhesive properties of the metal, resulting in its earlier accretion. It is difficult to explain (iv) in terms of a similar mechanism, unless it can be shown that enstatite has superior adhesive properties to olivine. Points (v) and (vi) depend on the proposed temperature changes during accretion of the enstatite meteorites. It is clear that if the proposed increase in temperature occurred subsequent to the accretion, large amounts of S and K have actually to be expelled from the parent body in order to explain the observed mineral and chemical trends. Furthermore, this simple increase in temperature must be associated with a change in redox conditions deep into the interior of the parent body in order to allow the adjustment of Si content of the kamacite to take place. Type I enstatite chondrites, which, in terms of the model, are located at the centre of the parent body, must have escaped this heating process. If, on the other hand, the increase in temperature postulated by Wasson and Wai is assumed to take place during the accretion process, explanation of points (v) and (vi) is less difficult. Under these conditions, the condensation of alkalis is partially, and increasing inhibited as condensation proceeds and temperatures increase, and secondly, mineral compositions at the accretion surface and in the unaccreted dust change in response to the increased temperature. Each successive layer of the parent body is thus equilibrated (except the Type I core) and different from previous layers due to the higher accretion temperature.

The model of Wasson and Wai appears to provide a satisfactory explanation of the observed chemical trends within the enstatite meteorites, although it cannot satisfactorily explain the presence of Ti in the silicate fraction in association with a high and uniform content of Si in the kamacite in Type I enstatite chondrites. However, it is difficult to conceive of any process which could explain the anomalous behavior of Ti.

Under conditions of formation such as postulated by Wasson and Wai, the inclusion of the chondritic fragment in Cumberland Falls is not unexpected. In fact, it is surprising that such polymict breccias are not more common (e.g. as was seen to be the case for the howardites).

5. Implications of enstatite chondrite - achondrite association for stony meteorite classification.

The genetic sequence extending from Type I enstatite chondrites through to enstatite achondrites poses some problems for the classification of stony meteorites. In terms of this sequence, enstatite achondrites and enstatite chondrites should be included within one group. Under such circumstances, the Si/Mg ratio can no longer be used to cate~~r~~gorize the enstatite group, as is done in the van Schmus and Wood (1967) system, since the Si/Mg ratio of the combined chondrites and achondrites encompasses the H, L and much of the C groups as well. Furthermore, it poses difficulties for the van Schmus and Wood concept of'petrologic types'. The chemical changes through the enstatite sequence are accompanied by textural changes, notably recrystallization (Mason 1966, Wasson and Wai 1970), and thus lend themselves to a petrologic grouping. However, the objections of Keil (1968) to the suggestion that this textural gradation is the result of metamorphism are now amplified by the gross chemical changes which are observed over the whole sequence. Furthermore, six sub-groups (i.e. E1 - E6) are not sufficient to encompass the enstatite achondrites as well as the chondrites.

In order to accomodate the enstatite achondrites with the chondrites in a genetically meaningful classification will require complete restructuring of the classification systems available at the present time.

THE HL CHONDRITES

The HL or Type III carbonaceous chondrites is a particularly interesting group of meteorites as far as their content of refractory elements is concerned, in particular Ca and Al. Within this group, significant variations in Ca and Al do occur, which are independant of dilution effects by volatile material. In spite of these variations, it appeared from earlier work (Ahrens and von Michaelis 1969a, Ahrens 1970c) that the Ca/Al ratio remained constant over the entire range of Ca and Al abundance.

This study was undertaken in an attempt to document the low abundance end of the Ca/Al ratio more precisely, and possibly to ascertain whether or not fine-structure exists in the Ca/Al ratio at these low levels.

1. Classification.

The development of the present day classification of the HL chondrites is briefly reviewed, as it bears some relevance to the chemistry of these meteorites. A variety of criteria for the classification and further sub-division of the HL or Type III carbonaceous chondrites have been put forward. Wiik (1956) suggested sub-division of what are now known as the carbonaceous chondrites on a basis of carbon and water content, with the Type III's containing least of these components. Mason (1962) saw Wiik's Type III as being a distinct class which he called the 'olivine - pigeonite ' chondrites. Following Mason (1963c) the use of the term 'Type III' appears to have been preferred. Subsequently, Keil and Fredriksson (1964) suggested the term HL chondrites for these meteorites, H denoting the high Fe group of Urey and Craig (1953) and L the low metal content. Van Schmus and Wood (1967) grouped all of Wiik's carbonaceous chondrite types together because of their similar Si/Mg ratio. In their classification system, the different sub-groups were recognized as 'petrologic types', with most Type III's being regarded as members of the C3 petrologic type, some as C2 and some as C4. More recently, van Schmus (1968) has recognized two distinct textural types within the HL chondrites, distinguishable on a basis of their chondrule morphology. These groups have been named after typical members of each type, and are termed the Ornans sub-type and the Vigarano sub-type.

2. Chemical features of the HL chondrites.

The HL chondrites, quite unlike other chondrite types (except the E group), show some significant variations in composition which seem to correlate with their petrography. The average Si/Mg ratio of the HL chondrites obtained in this work (1.07) is slightly lower than the value obtained by von Michaelis (1969) (1.10), although the difference is not regarded as significant. The Si/Mg ratio of the group as a whole is relatively uniform, and is virtually indistinguishable in the Vigarano and Ornans sub-types (Table 47).

However, if one considers the petrologic types of van Schmus and Wood (1967), it is evident that the C4 group has a slightly lower Si/Mg ratio than that of the C3 and C2 groups. More significant, however, is the Ca/Al ratio. As was pointed out in an earlier section, the Ca/Al ratio amongst the HL chondrites is not uniform, but appears to differ slightly in different groups. Thus, the Ca/Al ratio of the Vigarano sub-type in general appears to be lower than that of the Ornans sub-type (Table 47), but even more significant is the markedly lower Ca/Al ratio in the C4 group relative to the C3 and C2 groups. Surprisingly, these distinct differences in the Ca/Al ratio show no correlation with Ca and Al abundance. The C4 chondrites have abundances of Ca intermediate between the other two groups (Table 47).

TABLE 47

Classification[+]	Meteorite	Si/Mg	Ca/Al	%Ca	%Fe	Kppm
C4(?)-V	Leoville	1.05	0.98	1.80	22.02	100
C4-V	Coolidge	1.05	0.99	1.66	24.00	129
C3-V	Vigarano	1.06	1.09	2.26	22.24	319
C2-V	Mokoia	1.07	1.10	2.00	22.59	306
C3(?)-V	Allende	1.06	1.06	1.84	23.55	300
C3-O	Lancé	1.09	1.13	1.53	24.65	397
C3-O	Warrenton	1.06	1.12	1.57	25.43	390
C3-O	Felix	1.08	1.12	1.54	25.30	371

[+] C2, C3 and C4 denote the petrologic types of van Schmus and Wood (1967), and V and O the Vigarano and Ornans subtypes of van Schmus (1968) respectively. Classification from Clarke et al (1971).

The abundance of K in the HL chondrites is of particular interest. Examination of the data in Table 47 shows K to differ distinctly on the one hand between the Vigarano and Ornans sub-types, and on the other between the C4 and C3 petrologic types. A positive correlation exists between the K contents of HL chondrites and their Ca/Al ratios if only group averages are used. No correlation exists within a group. Likewise, Na shows a similar pattern to that exhibited by K (table 17) although certain anomalies exist - probably a reflection of the poorer quality of the Na data.

The element Fe, by contrast, shows a slight difference in abundance between the Ornans and Vigarano sub-types, being slightly lower in the latter group (see Table 47). Fe, however, is indistinguishable between the C3 and C4 groups.

3. Implications of inter-element relationships in HL chondrites.

It is clear from the above discussion that both Coolidge and Leoville are distinctly different from other HL chondrites as far as their bulk composition is concerned. Of the HL chondrites studied in this work, only these two are finds. The lower Ca/Al ratios and K and Na contents of these meteorites may reflect terrestrial weathering processes. However, both are highly recrystallized and hence extremely impervious. Examination prior to crushing showed no evidence of discoloration by Fe oxides within the samples, suggesting that, in general, weathering was only superficial. Thus, the chemical features referred to above are probably chacteristic of the meteorites themselves.

The only distinct chemical differences observed between the Vigarano and Ornans subtypes are lower K and Fe contents in the former group of meteorites. This suggests that Fe and K, like the rare gases, are associated more with the chondrules than the matrix, as van Schmus has indicated that the Ornans sub-type contains less matrix and is richer in rare gases than the Vigarano sub-type. More analyses would be required to establish whether the Ca/Al and Si/Mg ratios are significantly different between the two groups. The absolute Ca and Al abundances do seem to differ slightly between the two groups, with the Vigarano sub-type containing slightly more of these elements. However, no marked hiatus separates them. The conclusion of van Schmus (1968) that in the formation of both types, essentially the same parent material was subjected to differences in the chondrule-forming processes seems to be confirmed by these observations. These processes probably caused the slight differences in Ca, Al, Fe, Na and K between the two types.

It is clear from the foregoing discussion that superimposed on the slight chemical differences associated with the Vigarano and Ornans sub-types are marked chemical differences which correlate with petrologic type. Unfortunately, Karoonda, the only Ornans C4 representative thus far recognized, was not available for study. An examination of the K content and the Ca/Al ratio of this meteorite should prove interesting. In spite of this, it would appear from the data listed in Table 47 that the processes which led to the recrystallization of the C4 chondrites produced significant chemical differences between them and the relatively unrecrystallized C2 and C3 types. In this regard, a closer examination of the Ca (and Al) abundance is instructive. If only the C2 and C3 petrologic types are considered, it is clear that the Vigarano sub-type is separated from the Ornans sub-type by an hiatus in the Ca (and Al and Ti) content. This is filled by the C4 Vigarano sub-type members. If these C4 meteorites formed by the recrystallization of a normal C2 or C3 Vigarano sub-type member, then it would appear that Ca and Al have been lost during this process, and to different extents. Similarly, the somewhat old analysis of Karoonda (Mason and Wiik 1962) shows this meteorite to contain 1.50 % Ca, slightly lower than the C3 Ornans sub-type representatives studied in this work. (Wiik's Al analysis was performed using 'classical' techniques, and is probably unreliable).

If the processes which led to the observed chemical changes associated with the recrystallization of HL chondrites was metamorphic in character, as implied by van Schmus and Wood (1967), van Schmus (1968) and van Schmus (1969), for example, it is clear that such metamorphism was not isochemical, but led to the loss of Ca relative to Al, and of Na and K, with the latter two elements being reduced to one third of their original abundance. The transference of this material could conceivably have occurred simultaneously with the dehydration of these meteorites. Fe remained unaffected by these processes. Thus, C4 and C3 and C2 representatives of the Vigarano sub-type are indistinguishable on a basis of their Fe content, while this group as a whole may be distinguished from the Ornans sub-type by the Fe content. (see Table 47). This conclusion is supported by the reported Fe content of 25.55 % in Karoonda (Mason and Wiik 1962).

The location of Na, K and Ca in the HL chondrites is not clear. According to the work of Clarke et al (1971) on the Allende meteorite, it would appear that most of the Ca, Al, Na and K in HL chondrites occurs in the matrix material, although the matrix is composed largely of olivine. It is not clear whether these elements are in a form ameanable to removal by water.

From the foregoing discussion, it cannot be stated with any certainty whether the chemical differences between the C4 and C2 and C3 types is the result of metamorphic processes or occurred as a result of the formation of C4 chondrites at higher temperatures than C2 and C3 varieties as suggested for example by Kurat (1968). Suffice it is to say at this stage that the C4 petrologic grade of the C group chondrites appears to be associated with chemical differences from other C representatives in the form of lower Ca/Al ratios and lower absolute abundances of Ca, Na and K.

4. Some thoughts on the Ca/Al ratio.

Ahrens and von Michaelis (1969a) observed that the Ca/Al ratio in chondrites varies between very narrow limits. Ahrens (1970c) drew attention to the fact this ratio was invariant in spite of changes in the mineralogy and bulk chemistry. Further, the average Ca/Al ratio of 1.08 found by Ahrens and von Michaelis (1969a) is significantly greater than the maximum permissible ratio in anorthite of 0.74.

The study of the HL chondrites undertaken in this work has shown that significant variations in the Ca/Al ratio do occur in these meteorites, and appear to be associated with the recrystallization process. In view of the possibility that this could be a secondary phenomenon, i.e. one which occurred after the accretion of these meteorites, the original observations of Ahrens and von Michaelis on the constancy of this ratio still stand. The observed differences in Ca/Al ratio between the unrecrystallized Vigarano and Ornans subtypes is slight, compared to the differences in absolute Ca and Al abundance between these groups. In fact, this general constancy of the Ca/Al ratio could be regarded as evidence supporting the theory that metamorphism was responsible for the lower Ca/Al ratio and perhaps the other chemical perculiarities of the C4 chondrites.

The constant Ca/Al ratio observed in chondrites and possibly eucrites, must have implications regarding the formation of these meteorites.- particularly on the processes operative during the fractionation of elements in the nebula. Quite obviously, Ca and Al have not been relatively fractionated.

The form in which Ca and Al condensed from the nebular gas is of some interest. Larimer and Anders (1970) have suggested that Al and Ca condensed either as a single compound or as a mixture of compounds. With regard to the former suggestion, i.e. a single compound was responsible, it is clear that no simple stoichiometry could possibly produce a Ca/Al weight ratio of 1.08. Large atomic proportions are required to produce this ratio. Thus, atomic proportions of 11 Ca to 15 Al produce a weight ratio of 1.089. Compounds of such large stoichiometry do not appear in Larimer's (1967) list of compounds which are likely to form at high temperature in a nebula. It is doubtful whether a compound of such a high molecular weight could exist for any length of time at the temperatures at which condensation probably occurred. It thus seems unlikely that a single compound was responsible for the constant Ca/Al ratio. The inclusion of other refractory elements (e.g. Ti, Zr, etc) into a single, early-formed Ca-Al compound cannot be called upon to simplify the stoichiometry, as these elements are present in too low abundance. Thus the suggestion that a mixture of compounds was responsible seems more likely. It is clear, however, that these compounds must have condensed in balanced proportions, otherwise fractionation of the Ca/Al ratio would be observed. Alternatively, and more likely, all the Ca and Al in the nebula condensed, probably in a variety of forms, and the Ca/Al ratio observed in chondrites reflects that of the nebula.

SECTION V

CONCLUSION

One of the principal aims of the project was to investigate the possibility of fine-structure in the trends of enrichment of refractory elements through the chondrites, howardites and eucrites. Such fine-structure was indeed observed. The investigation indicated that enrichment of refractory elements in howardites does not imply a direct genetic link between these meteorites and chondrites, but relates to the complex genesis of howardites and eucrites.

The relationship between eucrites, a probable igneous differentiation product, and chondrites is not clear. Although the Ca-rich representatives of HL chondrites (Vigarano sub-type) could be construed as representing the parent material from which these meteorites formed (oxygen isotope evidence is not in conflict with this), on petrologic grounds this seems unlikely. Rather, the parent material of the eucrites and diogenites does not seem to be represented by any known meteorite. The Ca/Al ratio of eucrites may indicate that these are the products of differentiation of a magma enriched in high temperature Ca and Al rich (refractory) condensates from the nebula.

The unrecrystallized HL chondrites (i.e. C2 and C3) themselves appear to form two distinct compositional groups which coincide with the Vigarano and Ornans petrographic sub-types. The recrystallization which formed the C4 group appears to have been accompanied by chemical changes which have tended to obscure the compositional hiatus between the Ornans and Vigarano sub-types. It would appear that C4 meteorites represent normal C2 or C3 material which has been recrystallized.

The enstatite achondrites apparently form a genetic sequence with the enstatite chondrites. However, the relationship of these types with other chondrite types is not clear. The conclusions of Wasson and Wai (1970) that the absence of chondrules and a coarse grain-size do not necessarily imply melting are supported by the findings of this survey. The association of the enstatite achondrites and chondrites also creates problems in meteorite classification. The traditional chondrite-achondrite distinction is not valid in the case of these meteorites. Further, petrologic systems of classification will have to be revised as will the chemical criteria for recognizing groups, in particular the Si/Mg ratio.

Finally, it would appear that petrologic types in different meteorite classes have been produced by different phenomena. Thus, the C4 type was probably produced by metamorphism of C2 or C3 material, while the E5 or E6 meteorites do not seem to be metamorphosed equivalents of the E4 petrologic type .