

# HISTORY OF BOULDER 1 AT STATION 2, APOLLO 17 BASED ON TRACE ELEMENT INTERRELATIONSHIPS

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**Abstract.** Correlations among the trace and minor element pairs Cl and Br, Cl and  $P_2O_5$ , and Ru and Os, present in parent igneous rocks, generally survived the processes of boulder breccia formation.

Fractions of the Cl, Br, and Hg that are mobilized by water leaching and/or volatilization at moderate temperatures ( $\leq 450^\circ\text{C}$ ) place constraints on the thermal history of Boulder 1 and its component breccias. Since, and possibly during, consolidation, the boulder has probably not been subjected to temperatures of  $\geq 450^\circ\text{C}$ .

The parent rocks of the Apollo 17 boulder and breccia samples studied could have been derived from two initial magmas. Boulder 1, Station 2 gray competent breccias 72255 and 72275 Clast #2 appear to be genetically unrelated to gray competent breccia and anorthositic material 72215, or to light friable breccia 72275; they do appear to be related to samples 72395 (Boulder 2) and 76315 (Station 6 boulder).

Vapor clouds from apparently external sources permeated the source regions of the boulders.

## 1. Introduction

Labile trace elements F, Cl, Br, I, and Hg and non-labile trace elements Li, U, Ru and Os, and the  $P_2O_5$  contents have been determined in a number of Apollo 17 Boulder 1, Station 2, samples. The samples studied are listed in Table I. Our data on other massif samples, breccias 72395, 72417, and 76315 from other consortia and breccias 73275, 77035, and two lithologies in breccia 73235, are also presented but not considered in detail.

All samples were crushed but not ground or sieved in order to reduce the risk of contamination. Sample handling was done in a  $N_2$  dry box. For the halogen measurements the samples were first leached with hot  $H_2O$  for 10 min; the water soluble (leach) and insoluble (residue) fractions were determined and are designated with subscripts *l* and *r*. The data in Table II and the experimental procedure have been reported previously (Jovanovic and Reed, 1974a, b; 1975a). Our halogen data and that reported in the literature frequently disagree. The differences are usually just the amounts of Cl and Br we find in the leach (see Jovanovic and Reed, 1975b, for a discussion of Cl data in this regard). Additional Ru and Os data have been acquired for Boulder 1 samples and all the data for these two elements are given in Table III.

We shall examine the evolution of the Apollo 17 Boulder 1 and other lithic breccias from the point of view of trace element interrelations. The leachable fractions of the halogens Cl and Br will be proposed as possible vapor deposits; Br and Hg fractions volatilized in stepwise heating experiments will be used in thermal history considerations. The residual Cl and Br and  $P_2O_5$  will be used to suggest relationships or lack thereof among the various breccias; Ru and Os data will be considered in the light

TABLE I  
Description of Apollo 17 boulder and breccia samples<sup>a</sup>

*Boulder 1, consortium indomitabile*

72215,61	Gray competent breccia in slab, <i>GCBx</i> , (sugary dark).
72215,100	<i>GCBx</i> in knob.
72215,102	Anorthositic breccia, <i>AnBx</i> (gabbroic anorth.).
72255,61	<i>GCBx</i> (dark matrix breccia).
72275,66	Light friable breccia interior <i>LFBx</i> (light matrix breccia).
72275,110	<i>LFBx</i> exterior.
72275,161	Clast #2.

*Other Breccia Samples*

72395,43	tan-grey breccia matrix, Boulder 2, G. J. Wasserburg consortium
72417,1,1	interior } dunite, Boulder 3
72417,1,7	exterior } G. J. Wasserburg consortium
73235,48	medium light grey breccia, exterior and interior <i>dark</i> matrix and <i>white</i> clast.
73275,27	light grey breccia matrix.
76315,69	exterior with patina } green-gray breccia matrix Station 6 boulder
76315,70	interior } W. C. Phinney consortium
77035	light grey breccia matrix.

<sup>a</sup> Abbreviations used in text and tables are *italicized*. Descriptions used in our previous publications are in parentheses.

TABLE II  
Halogens, lithium, uranium, and P<sub>2</sub>O<sub>5</sub> in Apollo 17 boulder and breccia samples<sup>a</sup>

Sample	F ppm	Cl		Br		I <sup>c</sup> ppb	Li ppm	U ppm	P <sub>2</sub> O <sub>5</sub> wt %	
		<i>r</i> <sup>b</sup> ppm	<i>l</i> <sup>b</sup> ppm	<i>r</i> ppb	<i>l</i> ppb					
<i>Boulder 1</i>										
72215,100	<i>GCBx</i>	129	57	1.8	695	37	1.1	11	3.1	0.57
72215,102	<i>AnBx</i>	—	8.9	1.3	25	27	1.6	9.2	0.59	0.12
72255,61	<i>GCBx</i>	41	7.4	1.3	28	54	0.8	11	1	0.25
72275,110	<i>LFBx</i>	117 <sup>d</sup>	28	1.6	94	30	3.3	12	1.6	—
72275,161	Cl #2	77	28	0.9	370	25	1.5	8	2.7	0.6
72395,43	int. <sup>e</sup>	41	7.4	1.0	42 <sup>a</sup>	14 <sup>a</sup>	1.7	—	0.59	—
72417,1,1	int.	154 <sup>d</sup>	5.9	0.79	18	10	0.9	2.3	0.002	—
73235,48	white	—	17	4.8	58 <sup>a</sup>	100 <sup>a</sup>	4.4	8.1	0.48	—
73235,48	dark	30	17	3.0	58 <sup>a</sup>	57 <sup>a</sup>	1.9	5.5	1.2	—
73275,27		30	11	0.89	71	44	0.9	9.4	1.1	—
76315,69	ext. <sup>e</sup>	—	7.8	1.3	52 <sup>a</sup>	24 <sup>a</sup>	1.3	15	1.0	—
76315,70	int.	49	15	1.4	68 <sup>a</sup>	10 <sup>a</sup>	1.2	13	1.1	—
77035,82		39	9.6	1.3	15 <sup>a</sup>	12 <sup>a</sup>	1	7.1	0.83	—

<sup>a</sup> The counting statistical errors are usually 10% or less. Errors in Br are up to 30% in indicated samples. All data are from Jovanovic and Reed (1974a, b).

<sup>b</sup> *r* = residue after leaching; *l* = leach solution.

<sup>c</sup> I detected in leach only.

<sup>d</sup> Values for the interior sample 72275,66 and exterior 72417,1,7.

<sup>e</sup> int. = interior; ext. = exterior samples.

TABLE III  
Ruthenium and Osmium in Apollo 17 Boulder and Breccia Samples (in ppb)<sup>a</sup>

Sample			Ru	Os	Ru/Os	Ave Ru/Os
72255,61 <sup>b</sup>	GCBx	(4) <sup>c</sup>	≥ 20	17	≥ 1.2	
72275,66	GCBx	(9)	≤ 3	1.5	≥ 2	
72395,43	mtx.	(4)	17	9	1.9	meteoritic
72417,1,7	ext.		≤ 3	1.2	≤ 2.5	1.7
76315,69	ext.	(4)	6.7	4.7	1.4	
72215,100 <sup>b</sup>	GCBx	(9)	5.9	8.4	0.71	
72275,161 <sup>b</sup>	Cl #2	(4)	6.8	10	0.68	0.63 <sup>d</sup>
73235,48	int. dark	(9)	7.6	12	0.63	±0.07
76315,70	int.	(4)	6.3	12	0.53	
72215,61 <sup>b</sup>	GCBx		8	21	0.38	0.41 <sup>d</sup>
73235,44	ext. dark	(9)	5.3	14	0.38	±0.06

<sup>a</sup> Abbreviated sample descriptions are explained in Table I.

<sup>b</sup> New data.

<sup>c</sup> The number in parentheses refer to the Cl<sub>1</sub>/P<sub>2</sub>O<sub>5</sub> groups of 0.004-0.009; see Table V.

<sup>d</sup> Average Ru/Os ratio for 10 and 11 samples from Apollo 14, 15, 16, and 17.

of these relations. The Boulder 1 components have been subjected to various degrees of shock and brecciation, and to shock or burial-related heating and compression. These conditions might have affected trace elements and tended to modify or obliterate the original distributions. Except for the readily volatile Br and Hg fractions this *does not* appear to have been the case, as the following discussion will indicate.

## 2. Inter-Element Relations

### 2.1. LEACHABLE Cl AND Br

We have reported (Jovanovic and Reed, 1975a) that the H<sub>2</sub>O-soluble Cl and Br in lunar samples of all types tend to fall into groups with ratios (*R*) of ~20, 40, and 80. Two other groupings average ~160 and ~340. The *R* ~40 and 80 groups are the largest and have standard deviations of ~10% and 15%, respectively. They also contain most of our Apollo 17 breccia samples (Table IV). Four of five samples from Boulder 1 fall in the *R* ~40 group.

We have suggested that these halogen deposits resulted from vapor clouds external to the breccias. Such clouds could be associated with the processes that brought together the materials that now constitute the boulders. Since many other samples from a variety of sites have similar coatings it must be assumed that the number of events and/or sources of the released vapors was limited. Alternatively it is possible that the deposits were actually volatiles cooked out of the breccia components in their present locations in the boulders. The greater lability of Br would favor its exsolution relative to Cl and could account for the lower Cl<sub>1</sub>/Br<sub>1</sub> ratio on surfaces. It is not obvious, however, why Apollo 17 breccia samples which contain Cl<sub>1</sub> and Br<sub>1</sub> in ratios of ~80, 170, and 300 (see below) should all exsolve these elements to produce a deposit on surfaces with a ratio of 49 ± 7 (std. dev.) (see also Section 3).

TABLE IV  
Ratios of water soluble Cl and Br<sup>a</sup>

~ 20	Cl <sub>t</sub> /Br <sub>t</sub> ~40	~ 80
72255 GCBx	72215 GCBx	72395 mtx.
73275 mtx.	72215 AnBx	72417 dunite
	72275 LFBx ext.	77035 mtx.
	72275 Cl #2	
	73235 white	
	73235 dark	
	76315 ext. <sup>b</sup>	

<sup>a</sup> Abbreviated sample descriptions are explained in Table I.

<sup>b</sup> 76315,70 int. has Cl<sub>t</sub>/Br<sub>t</sub> ~ 140.

## 2.2. RESIDUAL Cl AND BR AND NON-LABILE TRACE ELEMENTS

The residual Cl<sub>r</sub> and Br<sub>r</sub>, Cl<sub>r</sub> and P<sub>2</sub>O<sub>5</sub>, and the Ru and Os relationships in the samples were all probably established by early magmatic processes, with possible modification by subsequent thermal events.

(1) The Cl<sub>r</sub>/Br<sub>r</sub> ratios for the Apollo 17 breccia samples measured fall into three groups with average values of ~80, 175 ± 32 and 306 ± 32, Table V. Sixty percent of all lunar samples measured have Cl<sub>r</sub>/Br<sub>r</sub> between 30 and 120, with a median of ~75. There are strong indications that there is structure within this range of Cl<sub>r</sub>/Br<sub>r</sub> ratios,

TABLE V  
Apollo 17 boulder and breccia sample groupings based on their residual and Cl<sub>r</sub>/Br<sub>r</sub> Cl<sub>r</sub>/P<sub>2</sub>O<sub>5</sub> ratios<sup>a</sup>

~ 80	Cl <sub>r</sub> /Br <sub>r</sub> ~ 170	~ 300
72275 Cl #2 (4) <sup>b</sup>	72395 mtx. (4)	72275 LFBx (9)
72215 GCBx (9)	73275 mtx. (4)	72255 GCBx (4)
	76315 ext. (4)	72215 AnBx (9)
	76315 int. (4)	72417 dunite
		73235 dark (9)
		73235 white (9)
Cl <sub>r</sub> /P <sub>2</sub> O <sub>5</sub>		
~ 0.004		~ 0.009
72255 GCBx		72215 GCBx
72275 Cl #2		72215 AnBx
72395 mtx.		72275 LFBx
73275 mtx.		73235 int. dark
76315 int.		
77035 mtx.		

<sup>a</sup> Abbreviated sample descriptions are explained in Table I.

<sup>b</sup> The numbers in parentheses refer to the Cl<sub>r</sub>/P<sub>2</sub>O<sub>5</sub> groups of 0.004, 0.009, above.

but this will not be discussed here. If the mean ratio of  $\sim 75$  is considered typical then the higher ratios of 175 and 300 may be attributed to a Br deficiency. The suite of samples from Boulder 1 may provide some insights. Processes such as thermal mobilization of labile elements could have been a factor. However, this could not have occurred after consolidation of the breccias, that comprise the boulder, or of the boulder itself. Boulder GCBx samples 72275 Clast # 2 (Cl # 2), 72215 matrix, and 72255 matrix, which are similar chemically (Blanchard *et al.*, 1975) and petrologically (Ryder *et al.*, 1975), have dissimilar  $\text{Cl}_r/\text{Br}_r$  ratios of  $\sim 80$  and  $\sim 300$ . The clasts within the matrices (72215 AnBx in 72215 GCBx matrix; 72275 Cl# 2 GCBx in 72275 LFBx matrix) do not present a consistent picture; in one case the matrix (72275) and in the other case the inclusion (72215 AnBx) appear to have lost Br. The confusion is probably best rationalized by assuming that the ratios were established prior to or during consolidation of the breccias that constitute the sampled layers of Boulder 1.

(2) We have reported that most lunar samples measured fall into Ru/Os groups of  $0.63 \pm 0.07$  and  $0.41 \pm 0.06$  (std. dev.) (Jovanovic and Reed, 1974a). Some of the Apollo 17 breccias fall into these same groups; the remainder appear to cluster near the meteorite ratio of 1.7. For Boulder 1 samples, the Ru/Os ratios parallel those for  $\text{Cl}_r$  and  $\text{Br}_r$ : 72275 matrix and 72255 matrix fall in the group with the meteoritic ratio, and 72275 Cl # 2 and 72215 matrix have another ratio (Table III). Thus, 72275 Cl # 2 contains a Ru-Os complement that is different from that in the 72275 matrix. If the various Ru/Os ratios are the result of chemical fractionation, differing conditions must have prevailed in order to account for the variations in the ratios and, as in the case of  $\text{Cl}_r$  and  $\text{Br}_r$ , must have been imposed prior to consolidation of the breccias and boulders.

(3) Support for an early establishment of trace element distributions with little or no subsequent modification is found in  $\text{Cl}_r\text{-P}_2\text{O}_5$  data. We have suggested a model for the early lunar crustal evolution based on  $\text{Cl}_r\text{-P}_2\text{O}_5$  systematics, implied stoichiometry, and the assumption that these elements were present exclusively in late residual liquids (Jovanovic and Reed, 1975b). Most of the samples we have analyzed fall into one of three  $\text{Cl}_r/\text{P}_2\text{O}_5$  groups with weight ratios of  $0.021 \pm 0.004$ ,  $0.009 \pm 0.001$ , and  $0.004 \pm 0.001$ . We have referred to these groups as 'liquids'. Basaltic and anorthositic samples appearing in each 'liquid' are assumed to be related as complementary members of differentiation sequences. Apollo 17 samples appear in all three  $\text{Cl}_r/\text{P}_2\text{O}_5$  groups. Apollo 17 basaltic samples occur in the group with a  $\text{Cl}_r/\text{P}_2\text{O}_5$  ratio of 0.021, which includes Apollo 16-Cayley samples as the  $\text{Al}_2\text{O}_3$  rich complement; some Apollo 17 breccias occur as KREEPy intermediate members of a sequence with Apollo 11 basalts and Apollo 16-Ray samples as end members, all with  $\text{Cl}_r/\text{P}_2\text{O}_5$  of 0.009; and other Apollo 17 non-mare breccias occur as complements to Apollo 12 and 15 basalts, with a ratio of 0.004.

The Apollo 17 Boulder 1 samples fall in the 0.004 and 0.009 groups; most other Apollo 17 breccias measured also fall into these two groups (Table V). If our premise is correct that these ratios are related to early magmas, we conclude that components

comprising 72255 matrix and 72275 Cl # 2, both GCBxs, were derived from a different source than those comprising 72215 GCBx and AnBx and 72275 LFBx; i.e. 72275 Cl # 2 is truly exotic to 72275 matrix.

When the element pairs in all the Apollo 17 breccias measured are considered, it appears that the Cl<sub>r</sub>-Br<sub>r</sub> and Ru-Os trends may have been established at an early time and modified in only a few cases. That is, the Cl<sub>r</sub>/P<sub>2</sub>O<sub>5</sub> group of 0.009 contains most of the samples with Cl<sub>r</sub>/Br<sub>r</sub> of ~300 and the fractionated Ru/Os groups (0.63 and 0.41); the 0.004 Cl<sub>r</sub>/P<sub>2</sub>O<sub>5</sub> group contains most samples with Cl<sub>r</sub>/Br<sub>r</sub> of ~160 (not discussed) and the primitive (meteoritic) Ru/Os group.

### 3. Thermal Constraints

Results from Br and Hg released during stepwise heating of Boulder 1 matrix samples may place constraints on the thermal history of the boulder. The details of these experiments will be reported elsewhere. In GCBxs 72215 and 72255 the total Br released during heating to 1200°C was comparable to that found in hot water leaching of the samples. The 72275 LFBx samples were not compared since exterior and interior pieces were used in leaching and stepwise heating experiments, respectively.

The release patterns for the three samples, including 72275 LFBx, are quite different from one another (Figure 1). About 60% of the volatile Br in 72215 (16 ppb) and 72255 (34 ppb) was released at temperatures up to 175°C; only a few percent was released in 72275 (<0.1 ppb), in which >90% (~1 ppb) of the Br volatilized between 175 and 450°C. The release patterns indicate that the labile Br is present in a number of sites and/or types of compounds.

In our experience Hg is completely released when samples are heated to melting. The release patterns for Hg are unlike those for Br in these samples. The amounts and percentages of Hg released in the various temperature intervals varied widely among the three matrix samples. The variation in the lowest temperature intervals (130 and 175°C) is discounted as possibly due to lunar atmospheric Hg (Reed *et al.*, 1971); i.e. Hg ambient at sub-solar temperatures (~130°C). The Hg concentrations in the 130- or 175-450°C interval are of interest in terms of the thermal history of the boulder. Although Hg diffusion studies have not been made on lunar samples as yet, experience with meteorites indicates that this fraction of Hg is mobilized with a low activation energy and probably migrates by diffusion along grain boundaries, pores, or defect structures. The differences in the concentration of this Hg in Boulder 1 samples could imply that the boulder was not sustained at a sufficiently elevated temperature to cause concentration equilibration of this Hg throughout the boulder. Saturation of grain surfaces can probably be ruled out as a factor since the Hg concentrations are low.

The apparent failure of Hg to become uniformly distributed, i.e. mobilized, would appear to preclude the loss of Br from inside grains by heating as a possible way of accounting for the increase in Cl<sub>r</sub>/Br<sub>r</sub> ratios from ~80 for 72215 to ~300 for 72275 and 72255.

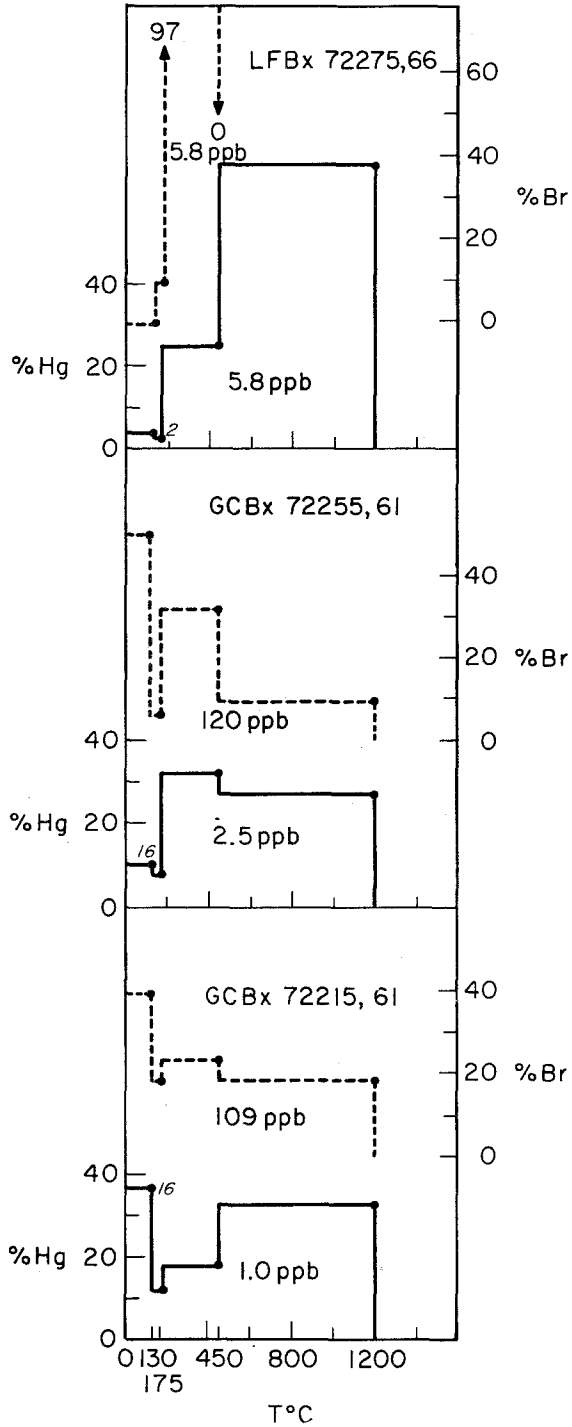


Fig. 1. Release patterns of Hg and Br on stepwise heating. Fractions were taken at one hour intervals, unless indicated otherwise (hours in italics). Total concentrations released are indicated.

The stepwise heating results can be used to propose a partial temperature history for Boulder 1 constituents. This is highly speculative and may have to be revised when diffusion studies have been carried out or even when different samples are measured. An appreciable fraction (25–65%) of the Hg in the samples is released between 450 and 1200°C. This high temperature component probably became trapped before the boulder was assembled. Subsequent to assemblage, the boulder could not have attained or alternatively sustained moderate (up to ~450°C) temperatures for long periods of time, since the relatively mobile 175–450°C fractions indicate no equilibration throughout the boulder. A temperature gradient as a cause for variations would not be expected across the boulder. The very labile (<175°C) Hg, which could have been present, would provide a reservoir for the Hg diffusing along grain boundaries. However, the lunar atmosphere cannot be ruled out as the source of this low-temperature Hg in the samples (Reed *et al.*, 1971) since the most exposed rock, 72275, (top of boulder) is the most depleted in this Hg (and Br) fraction.

A boulder history such as suggested is quite consistent with the thermal and temporal history proposed by Banerjee and Swits (1975). On the basis of magnetic studies they report a two-stage evolution; the earlier magnetizing event was pre-consolidation and at high temperature (~770°C), and the second was post-consolidation with magnetization occurring at a lower temperature (~450°C). If this latter stage was of short duration, the 450°C temperature may not pose a problem for our volatile element distributions.

#### 4. Conclusions

(1) The parent rocks of the breccia constituents in Boulder 1 were derived from at least two early magmas. The relationships among the incompatible elements were not completely irradiated or modified in the processes of rock crystallization, brecciation, transport, and incorporation into breccias with concurrent or subsequent heating and induration.

(2) The 72255 and 72275 Cl # 2 gray competent breccias are genetically unrelated to 72275 light friable breccia and 72215 gray competent or anorthositic breccia. If, as suggested, 72275 Cl # 2 is exotic to 72275 matrix, it must have been incorporated into this matrix in an early event; the breccia then evolved through the Curie point at a time when magnetic fields were present (Banerjee and Swits, 1975).

(3) Trace element concentrations and distributions in components of the breccias were apparently acquired early, prior to Boulder 1 formation. The boulder itself was not subjected to more than moderate heating (probably 450°C) and certainly not to sustained heating.

(4) Samples from the 72215 and 72275 rocks have the same relative amounts of Cl<sub>1</sub> and Br<sub>1</sub> on their surfaces. Sample 72255 from the same boulder contains a deposit of different composition. The surface coating of this sample would seem to require deposition at a different place or under different conditions.

External vapor clouds permeating the formations from which the boulders were derived could account for the uniform surface deposits. Such a vapor cloud could



be related to the stream of gases that sculptured surfaces as described by Marvin (1975).

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