

Sr/Ca–Ba/Ca SYSTEMATICS IN ANTARCTIC Ca-RICH ACHONDRITES AND THEIR ORIGINS

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Abstract: The Ca, Sr and Ba contents of six Antarctic polymict eucrites (Y-74450, Y-75011, Y-75015, ALH-765, ALH-78040 and ALH-78132) and a unique Antarctic achondrite (ALH-77005) have been determined by ICP-OES. When the data are plotted in the Sr/Ca–Ba/Ca diagram which enables us to visualize igneous processes such as partial melting and crystal fractionation, the eucrites fall on a crystal fractionation line defined by a set of typical eucrites and the unique achondrite falls on a partial melting line through chondritic Sr/Ca and Ba/Ca ratios. The results suggest that the eucrites are a series of melts evolved from a primary magma by clinopyroxene and plagioclase fractionation, while the unique achondrite is a residual solid phase derived from a chondritic source material by a large-scale partial melting.

1. Introduction

Recently, ONUMA (1980) proposed a new diagram, “Sr/Ca–Ba/Ca diagram”, which is considered to have a potential ability for analysis of magma genesis. The diagram is applicable, not only to volcanic rocks generated on the surface of the Earth, but also to the igneous rocks collected from the Moon and derived from a eucrite parent body.

In this paper, we report on the Sr/Ca and Ba/Ca ratios of six Antarctic polymict eucrites, Yamato-74450 (TAKEDA *et al.*, 1979), Yamato-75011 (TAKEDA *et al.*, 1979), Yamato-75015 (TAKEDA *et al.*, 1979), Allan Hills-765 (MIYAMOTO *et al.*, 1979), Allan Hills-78040 (MASON, 1979), Allan Hills-78132 (MASON, 1979), and a unique achondrite Allan Hills-77005 (ISHII *et al.*, 1979), determined by an inductively coupled plasma-optical emission spectrometry (ICP-OES), and discuss about origin and evolution of these meteorites in the eucrite parent body, using the Sr/Ca–Ba/Ca diagram which has been constructed for meteoritic magma genesis.

2. Experimental

Each Antarctic meteorite sample (about one gram) was crushed in an agate mortar and fragments of fusion crusts were removed by hand-picking under a binocular microscope. 500 mg of the fragments were pulverized under acetone in an agate mortar,

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Table 1. Accuracy and precision of the ICP-OES method.

	Ca	Sr	Ba
Wave length (nm)	317.9	407.7	455.4
Dynamic range	10 ⁴	10 ⁵	10 ⁵
Detection limit (ppb)*	13	0.2	0.7
Analytical results of JB-1 (ppm)			
X	66900	439	493
σ	1010	7.6	9.0
Certified value**	66300	435	490

* Calculated as the concentration denoting 3σ of background intensity noise.

** Compiled by ANDO (1978).

dissolved in HF-HClO₄ mixture on a platinum dish, evaporated to dryness, taken up by 1 ml of HClO₄, then diluted to 100 ml.

The sample solution thus prepared was analyzed by ICP-OES, a Jarrell-Ash PLASMA ATOMCOMP model 975. The operating conditions were the same as those of our regular method (HIRANO *et al.*, 1980). The accuracy and precision of the method are summarized in Table 1. As shown in Table 1, the method has large dynamic range, low detection limit and high accuracy and precision so that we can get a set of coherent data from a given sample solution.

3. Results

The analytical results obtained by this work are shown in Table 2, for six Antarctic eucrites, Y-74450, Y-75011, Y-75015, ALH-765, ALH-78040, ALH-78132, and for a unique achondrite ALH-77005. As indicated in Table 2, the Ca, Sr and Ba contents in the unique achondrite (ALH-77005) are clearly different from those of the Antarctic eucrites.

Table 2. Ca, Sr and Ba contents of six Antarctic eucrites and a unique Antarctic achondrite.

	Ca (ppm)	Sr (ppm)	Ba (ppm)
Y-74450	68400	73.7	40.1
Y-75011	68500	74.5	40.5
Y-75015	70600	76.3	39.8
ALH-765	67300	71.5	33.8
ALH-78040	69400	72.8	32.6
ALH-78132	61100	62.7	30.5
ALH-77005	21000	6.2	2.4
	20200	6.3	2.3

4. Discussion

4.1. Sr/Ca–Ba/Ca diagram

Firstly, we would like to explain a new diagram as a possible indicator for magma genesis (ONUMA, in preparation, 1981). The diagram is called “Sr/Ca–Ba/Ca diagram” (SB diagram hereafter). The principle is schematically shown in Fig. 1.

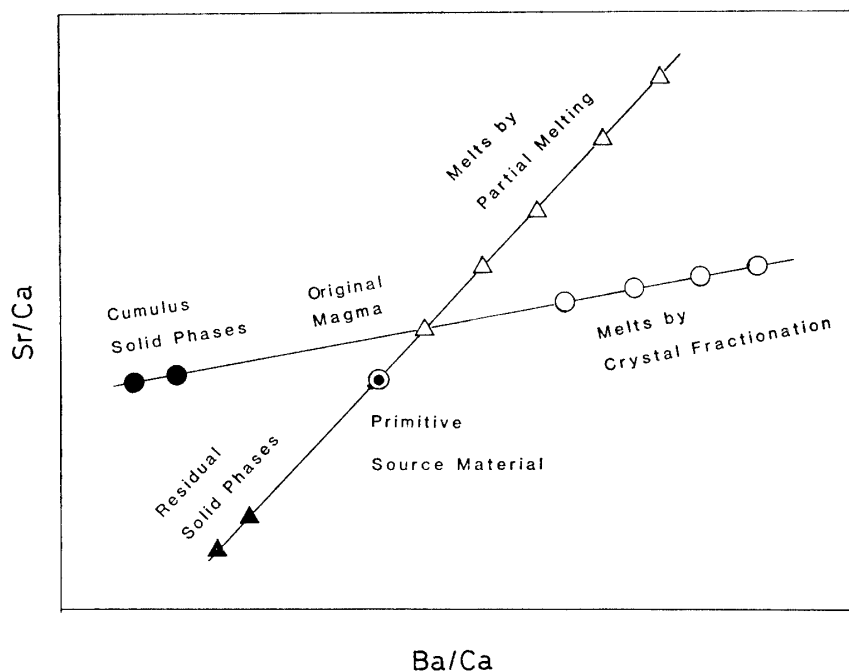


Fig. 1. Sr/Ca–Ba/Ca diagram as a possible indicator for magma genesis.

Large divalent cations, Ca^{2+} (1.00A), Sr^{2+} (1.17A), Ba^{2+} (1.36A) show different behavior in igneous processes controlled by structure of crystallizing mineral from silicate melt in magma (ONUMA *et al.*, 1968; HIGUCHI and NAGASAWA, 1969; JENSEN, 1973; MATSUI *et al.*, 1977). Therefore, the Sr/Ca and Ba/Ca ratios are considered to be sensitive geochemical indicators for elucidation of origin and evolution of magma.

Let us consider a primitive planetary material such as chondritic meteorites. Of these elements, Sr and Ba are contained, not in the major phases such as olivine, pyroxenes, metallic iron, and troilite, but in accessory minerals such as plagioclase and apatite and in the fine-grained interstitial materials. While, Ca is situated mainly in clinopyroxene and plagioclase.

When the original source material is gradually heated, partial melting occurs. Small degree of the partial melting produces strong enrichment of Sr and Ba in the melt, since plagioclase and the accessory phases are among the first components to enter into the melt. Increase of the degree of partial melting dilutes Sr and Ba contents

with the addition of Sr- and Ba-poor, major phases. The Sr/Ca and Ba/Ca ratios of the melt decrease with constant Sr/Ba ratio by addition of Ca from clinopyroxene. The melt evolved by complete melting of the original source material has the same Sr/Ca and Ba/Ca ratios with those of the original source material. Therefore, a series of melts derived from different degrees of partial melting of a common source material make a “Sr/Ca–Ba/Ca systematics” (SB systematics hereafter) in the SB diagram.

On the other hand, the residual phases (olivine, orthopyroxene, metallic iron and troilite) left over show low Sr/Ca and Ba/Ca ratios and they are located off the original source material on the SB diagram. Rather high contents of these elements suggest presence of small amounts of the melt in the residual phases. Therefore, again, we can expect a SB systematics from a series of the residual phases.

The SB systematics may be a line with a slope of 45° through the original source material, as schematically shown in Fig. 1. The line is actually a mixing line, since the Sr/Ca and Ba/Ca ratios are controlled by addition of Ca from clinopyroxene with a constant Sr/Ba ratio defined by that of plagioclase and the accessory phases.

Secondly, let us consider evolution of the once-generated melt by crystal fractionation. The Sr/Ca and Ba/Ca ratios of the melt change during crystal fractionation. For example, Ca enters into Ca-rich pyroxene, Sr is hard to enter, and Ba does not enter into the pyroxene controlled by crystal structure of the pyroxene (ONUMA *et al.*, 1968; MATSUI *et al.*, 1977). Therefore, the Sr/Ca and Ba/Ca ratios of the melt increase in the clinopyroxene fractionation. Increase of the Ba/Ca ratio is much larger than that of the Sr/Ca ratio in the melt. In the case of plagioclase fractionation, the Sr/Ca ratio in the melt does not change while the Ba/Ca ratio increases greatly, since plagioclase accepts both Ca and Sr with similar degree but excludes Ba by crystal structure control (HIGUCHI and NAGASAWA, 1969; MATSUI *et al.*, 1977). Therefore, a series of melts via clinopyroxene and plagioclase fractionation make another “SB systematics” with a gentle slope through the original magma as shown in Fig. 1. The slope is defined by the crystallizing minerals.

On the other hand, the Sr/Ca and Ba/Ca ratios of the cumulus phases separated from the original magma decrease gradually and rapidly, respectively. Again, we can expect a SB systematics from a series of the cumulus phases. The line shows the same gentle slope off the original magma, as shown in Fig. 1.

A summary of the proposed SB diagram as a possible indicator for magma genesis is as follows: there are at least two possible SB systematics; one is SB systematics derived from a series of melts by partial melting of original source material and its residual phases, the other is SB systematics derived from a series of melts by crystal fractionation of original magma and its cumulus phases. The intersection of the two systematics corresponds to the composition of the original magma generated from the original source material by partial melting.

4.2. Ca-rich achondrites on SB diagram

For constructing a SB diagram, it is essential to obtain a set of precise and coherent data for Ca, Sr and Ba from a set of given samples. Literature survey reveals that these data are rather scarce. Fortunately, TERA *et al.* (1970) have reported such data on nine Ca-rich achondrites including two cumulus achondrites such as Moore County (HESS and HENDERSON, 1949) and Angra dos Reis. The data were obtained by an isotope dilution method and have excellent quality.

Figure 2 shows a SB diagram for Ca-rich achondrites, using the data from TERA *et al.* (1970). Nine achondrites make a SB systematics with a gentle slope, suggesting

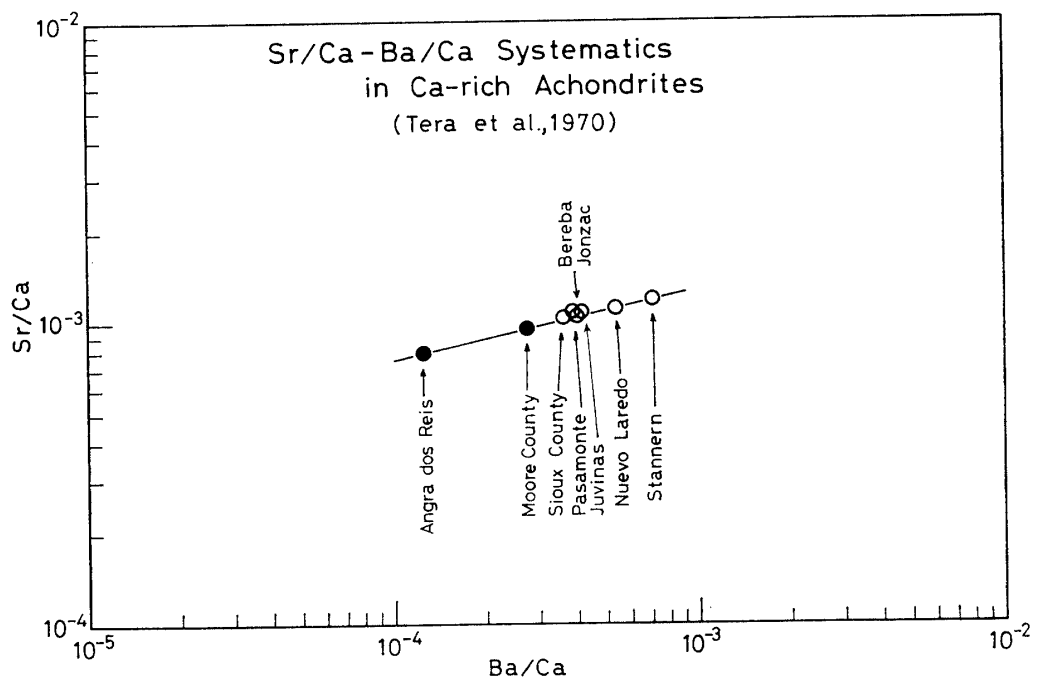


Fig. 2. *Sr/Ca-Ba/Ca systematics in Ca-rich achondrites* (○: normal eucrites; ●: cumulus achondrites; data from TERA *et al.* (1970)).

that seven eucrites (Sioux County, Bereba, Jonzac, Pasamonte, Juvinas, Neuvo Laredo and Stannern) are melts derived from a common original magma by crystal fractionation. Among these eucrites, Sioux County is the smallest and Stannern is the largest fractionation products in the crystallization process. Figure 2 also suggests that Moore County and Angra dos Reis are cumulus phases crystallized from the common original magma. The former may contain small amounts of melt in it, while the latter consists largely of Ca-rich violet pyroxene. The slope of the SB systematics is considered to be defined mainly by clinopyroxene and plagioclase. The original magma must fall on the SB systematics between Moore County and Sioux County achondrites.

4.3. *Eucrites and unique achondrite from Antarctica*

The three element plots for six polymict eucrites and one unique achondrite from Antarctica are given in Fig. 3. The six Antarctic eucrites (Y-74450, Y-75011, Y-75015, ALH-765, ALH-78040 and ALH-78132) fall on the SB systematics defined by the Ca-rich achondrites in Fig. 2, suggesting that the Antarctic polymict eucrites are a mixture of melt and cumulate derived from the common original magma by the same crystal fractionation process. However, the unique Antarctic achondrite, ALH-77005, is off the Ca-rich achondrite SB systematics line. How do we interpret the uniqueness on the SB diagram?

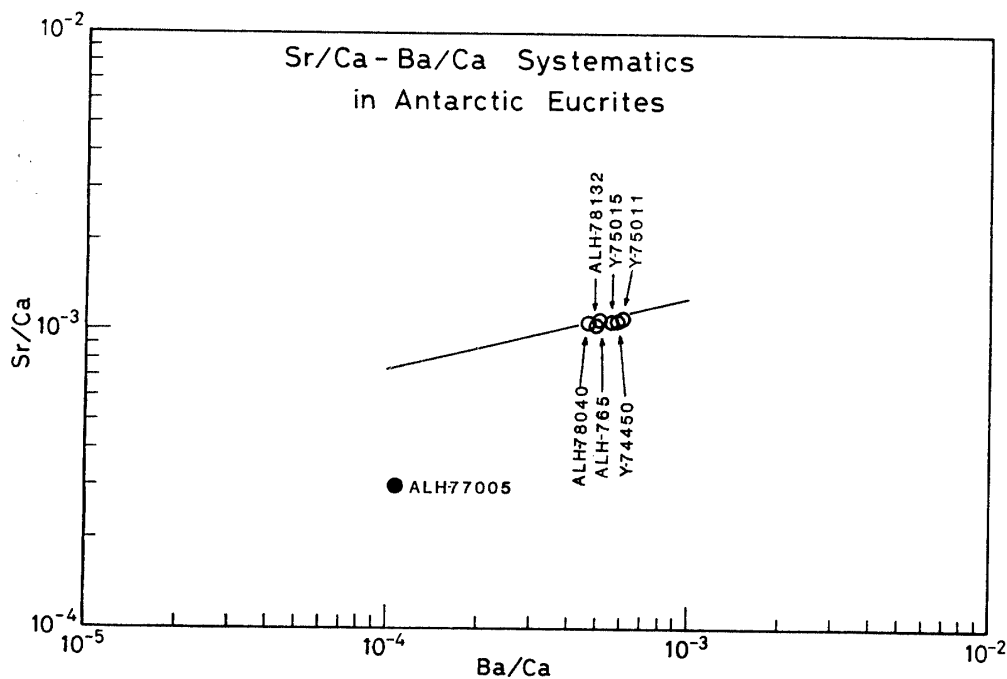


Fig. 3. *Sr/Ca–Ba/Ca systematics in Antarctic eucrites.*

A clue for the interpretation comes up from Fig. 4, in which a datum of Y-692 diogenite is plotted. The Ca content and the Sr and Ba contents in Y-692 diogenite are cited from SHIMA and SHIMA (1973) and MASUDA and TANAKA (1978), respectively. It should be noted that a line connecting ALH-77005 unique achondrite and Y-692 diogenite crosses the Ca-rich achondrite line between Moore County and Sioux County, as shown in Fig. 4. As stated in Subsection 4.1, the common original magma should be located between Moore County and Sioux County on the Ca-rich achondrite line. It should be noted that the line defined by three points (Y-692, ALH-77005 and the hypothetical original magma) show a slope of 45° , suggesting a mixing line derived from partial melting of the common original source material, as stated in Subsection 4.1.

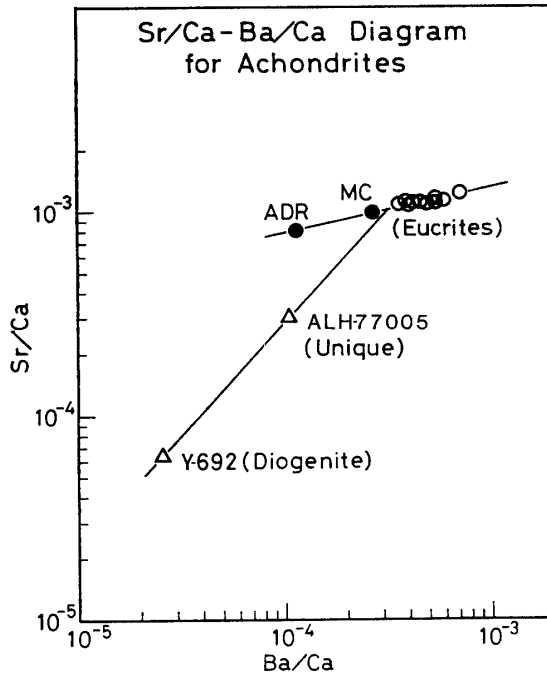


Fig. 4. *Sr/Ca-Ba/Ca* diagram for achondrites (○: normal eucrites; ●: cumulus achondrites; △: unique achondrite and diogenite; data from TERA *et al.* (1970), MASUDA and TANAKA (1978), SHIMA and SHIMA (1973) and this work.)

Thus, the unique achondrite, ALH-77005, is interpreted as a residual phase separated from the hypothetical original source material during partial melting. Figure 4 also suggests that the diogenite, Y-692, is also a residual phase separated from the hypothetical original source material.

4.4. *SB* diagram for meteorites

Finally, we would like to present a *SB* diagram for meteorites in Fig. 5 which is basically important to elucidate origin and evolution of the eucrite parent body in the early solar system. Chondritic meteorites (E, H, L and C chondrites) fall on the mixing line with a slope of 45° and occupy a place near but just under the Ca-rich achondrite line. The data are from TERA *et al.* (1970), SHIMA and SHIMA (1973) and MASUDA and TANAKA (1978).

Figure 5 suggests that the original source material from which the differentiated meteorites have evolved has a chondritic composition in terms of Sr/Ca and Ba/Ca ratios. The parent body would have been once melted with a large-scale partial melting, since the hypothetical original magma (intersection of the two lines) is situated close to chondritic meteorites. The original magma would have evolved through crystal fractionation process, as indicated by the Ca-rich achondrite *SB* systematics. The crystal fractionation process would be controlled by clinopyroxene and plagioclase crystallization, since the *SB* systematics show a gentle slope defined by a mixture of the two minerals. The eucrites are considered to be melts produced by two igneous processes, that is, partial melting and crystal fractionation.

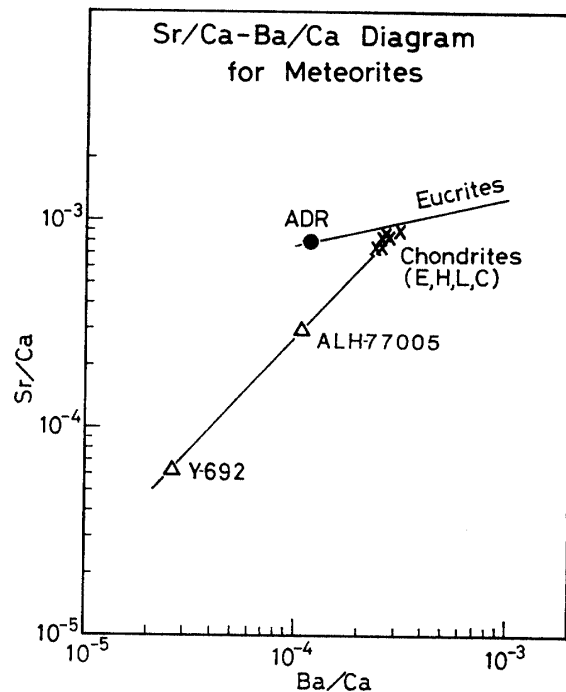


Fig. 5. Sr/Ca-Ba/Ca diagram for meteorites (Symbols are same as those in Fig. 4 except \times : chondrites; data from TERA *et al.* (1970), MASUDA and TANAKA (1978), SHIMA and SHIMA (1973) and this work.)

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References

- ANDO, A. (1978): Hyōjun ganseki shiryō-1978 (International reference rock samples-1978). *Bunseki*, **8**, 526-535.
- HESS, H. H. and HENDERSON, E. P. (1949): The Moore County meteorite: A further study with comment on its primordial environment. *Am. Mineral.*, **34**, 494-507.
- HIGUCHI, H. and NAGASAWA, H. (1969): Partition of trace elements between rock-forming minerals and the host volcanic rocks. *Earth Planet. Sci. Lett.*, **7**, 281-287.
- HIRANO, M., NOTSU, K. and ONUMA, N. (1980): Rapid simultaneous 17 elements analysis of some Yamato meteorites by ICP-OEC. *Mem. Natl Inst. Polar Res., Spec. Issue*, **17**, 152-158.
- ISHII, T., TAKEDA, H. and YANAI, K. (1979): Pyroxene geothermometry applied to a three-pyroxene achondrite from Allan Hills, Antarctica and ordinary chondrites. *Mineral. J.*, **9**, 460-481.
- JENSEN, B. B. (1973): Patterns of trace element partitioning. *Geochim. Cosmochim. Acta*, **37**, 2227-2242.
- MASON, B. (1979): Antarctic meteorite data sheet, sample No. ALHA78040; sample No. 78132. *Antarct. Meteorite Newsl.*, **2**(2), 5 and 7.
- MASUDA, A. and TANAKA, T. (1978): REE, Ba, Sr and Rb in the Yamato meteorites, with special reference to Yamato-691(a), -692(b) and -693(c). *Mem. Natl Inst. Polar Res., Spec. Issue*,

- 8, 229-232.
- MATSUI, Y., ONUMA, N., NAGASAWA, H., HIGUCHI, H. and BANNO, S. (1977): Crystal structure control in trace element partition between crystal and magma. *Bull. Soc. Fr. Mineral. Cristallogr.*, **100**, 315-324.
- MIYAMOTO, M., TAKEDA, H., YANAI, K. and HARAMURA, H. (1979): Mineralogical examination of the Allan Hills No. 5 meteorite. *Mem. Natl Inst. Polar Res., Spec. Issue*, **12**, 59-71.
- ONUMA, N., HIGUCHI, H., WAKITA, H. and NAGASAWA, N. (1968): Trace element partition between two pyroxenes and the host lava. *Earth Planet. Sci. Lett.*, **5**, 47-51.
- ONUMA, N. (1980): Inseki, tsuki, chikyû ni okeru Sr-Ba shisutematikkusu (Sr-Ba systematics on meteorites, the moon and the earth). *Solar System Science Symposium II*. Tokyo, The Institute of Space and Astronautical Science, University of Tokyo, 1-6.
- SHIMA, M. and SHIMA, M. (1973): Mineralogical and chemical composition of new antarctic meteorites. *Meteoritics*, **8**, 439-440.
- TAKEDA, H., MIYAMOTO, M., ISHII, T., Yanai, K. and MATSUMOTO, Y. (1979): Mineralogical examination of the Yamato-75 achondrites and their layered crust model. *Mem. Natl Inst. Polar Res., Spec. Issue*, **12**, 82-108.
- TERA, F., EUGSTER, O., BURNETT, D. S. and WASSERBURG, G. J. (1970): Comparative study of Li, Na, K, Rb, Cs, Ca, Sr and Ba abundances in achondrites and in Apollo 11 lunar samples. *Proc. Apollo 11 Lunar Sci. Conf.*, **2**, 1637-1657.

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