

"Rare Earth Abundances in Meteoritic Chondrules" †

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Introduction

The composition of individual chondrules is known for only a few elements from a few meteorites. Recently, the abundances of seven elements, Na, Sc, Cr, Mn, Fe, Co and Cu were measured by thermal-neutron activation analysis in 596 individual chondrules separated from 28 chondritic meteorites (Schmitt, et al, 1965; Schmitt and Smith, 1966). Abundances of Si have been determined in some 275 individual chondrules from 19 different chondrites via 14-Mev neutron activation (Schmitt, et al, 1967a). Microprobe, mineralogical, and isotopic analyses of selected chondrules and their grains were carried out by Fredriksson (1963), Keil and Fredriksson (1964), Wood (1963) and Merrihue (1963). The general conclusion that may be drawn from the above studies is that elemental abundances in chondrules agree fairly well with solar abundance values; however, since too few elements have been investigated, these conclusions must necessarily be regarded with reservations.

Several hypotheses suggest that chondrules predate whole rock chondrites and that chondrules may have condensed out of the primitive solar matter under high-temperature pressure conditions (Wood, 1963). Lightning discharges in the primeval solar nebula may have remelted dust grains in solar nebular

matter with subsequent chondrule formation on cooling (Whipple 1966). Larimer and Anders (1967) have discussed the implications of these hypotheses and others on origin of chondrules and chondrites.

The elemental abundance distribution of the 14 REE (rare earth elements), Y included, have been determined by RNAA (radiochemical neutron activation analysis) in 20 whole rock chondritic meteorites (Schmitt et al 1963, 1964, Haskin and Gehl 1962) spread over the three major chondritic groups, carbonaceous, ordinary and enstatite chondrites. Their data have been summarized by Haskin et al (1966). The most striking result was that the 14 RE relative abundances have remained essentially unchanged over the chondritic spectrum.

Upon appropriate normalization, Clayton et al (1961) have calculated theoretical RE abundances within their general framework of elemental nucleosynthesis. The agreement between the experimental chondritic RE abundances and the theoretical values was surprisingly good, considering the many assumptions involved in the complicated theoretical analysis.

Since this long and continuous series of non-volatile RE elements offers an excellent test for some aspects of nucleosynthesis models, the RE abundances must be investigated in any representative matter which has been seriously proposed in the development of the evolution of our solar system and for any matter that may have predated the chondrites per se.

Experimental

The 14 rare earth elements (REE) and Y were determined by radiochemical neutron activation analysis (RNAA) in 30 combined magnetic chondrules (0.079 g) from Mokoia (Type III carbonaceous chondrite), in 30 combined chondrules (0.080 g) from Chainpur (Un-equilibrated LL-group chondrite), in 35 combined chondrules (0.081 g) from Forest City (H-group chondrite), and in 50 combined chondrules (0.077 g) from Richardton (H-group chondrite).

Specific observations on the separation and characterization of these chondrules have been given elsewhere by Schmitt et al (1965, 1967b). In general, the chondrules that constituted the different batches were randomly picked; therefore, any elemental abundances should be truly representative and not deliberately biased.

The RNAA method was that previously described by Schmitt et al (1963) and Goldberg et al (1963). In short, two chondrule batches, in two polyethylene vials, were irradiated simultaneously with the 14 REE and Y standards in the rotating rack of the TRIGA reactor for two hours at a neutron flux of $1.8 \times 10^{12} \text{ cm}^{-2} \text{ sec}^{-1}$. After neutron irradiation, the chondrule batches were fused with appropriate RE carriers and Na_2O_2 . After radiochemical decontamination of the REE, the REE were separated by an ion-exchange column. The activity level of the individual REE, La, Sm and Eu were sufficient to permit γ -ray scintillation counting. The remainder of the REE and Y

were counted by a Sharp Lowbeta counter with a background of ≈ 0.3 cpm. Beta counting rates at ≈ 0.45 geometry varied from about 5 to 500^{cpm} above background.

Experimental Results and Discussion

Absolute abundances of the REE and Y have been tabulated in Table 1. For comparison, the normalized abundances (Haskin et al 1966) of the 14 REE and Y in 20 chondritic meteorites have been included in the last column of Table 1. The (+) values of the REE and Y for the chondrules represent the standard deviation principally due to counting statistics. For the last column in Table 1, the (+) values represent the mean deviation of the normalized values relative to Yb at unity.

In Figs. 1 and 2, the ratios of the respective normalized values in the chondrules to the average normalized values in 20 chondrites have been plotted versus the ionic radii of the REE.

From Table 1 and Figs. 1 and 2, the following observations are noted.

1. Total REE abundances in Mokoia chondrules are roughly twice those found in the whole chondrite, i.e., 12.5 ppm versus 6.9 ppm. For Chainpur, an unequilibrated LL-group chondrite, the RE absolute abundances in the chondrules are approximately equal to those determined in other whole-rock, ordinary L-group chondrites.

2. Total absolute abundances of the REE in Forest City and Richardton chondrules are less compared to the REE in the respective chondrites, i.e., 4.1 ppm REE in Forest City chondrules compared to 5.9 ppm in the whole-rock chondrite, and 3.7 ppm REE in Richardton chondrules versus 5.6 ppm in the corresponding whole-rock chondrite. For both batches of chondrules, about 30 percent less total REE reside in chondrules compared to the whole-rock. It is not known if the observed depletion of REE in chondrules from ordinary chondrites may be ascribed to a deficiency in chondrules caused by RE diffusion out of the chondrules during metamorphism or to specific minerals that occlude the REE, whatever the mechanism.
3. For Mokoia chondrules, a linear RE fractionation may be present, amounting to $\approx 20\%$ for La relative to Yb. Within experimental error, no significant RE fractionation occurs in Chainpur chondrules. From the accurately determined Sm/Eu ratios, Eu abundances in Mokoia and Chainpur chondrules are unchanged with respect to the adjacent REE.
4. A very significant linear fractionation of the REE has been observed for both Forest City and Richardton chondrules; for the former, La has been fractionated by $\approx 54\%$; for the latter, $\approx 45\%$. In both cases, the absolute abundance of Yb has decreased $\approx 10\%$ and $\approx 20\%$, respectively,

in Forest City and Richardton chondrules relative to Yb in the respective whole-rock chondrites.

5. For both Forest City and Richardton chondrules, Eu has been significantly fractionated with respect to the adjacent REE. The average Sm/Eu ratio of 2.7 ± 0.4 in whole-rock chondrites compares to 1.6 and 1.5 in chondrules from these two H-group chondrites.

Some obvious interpretations of the above RE fractionations involve diffusion of the REE and Y out of chondrules during metamorphism, as exemplified by the Forest City and Richardton data. The RE distribution in Mokoia and Chainpur indicates $\lesssim 20\%$ fractionation for La, the lightest REE; in fact, for Chainpur, almost all the error bars overlap unity, indicating little fractionation. Since Mokoia and Chainpur chondrules are certainly more primitive and unequilibrated than Forest City and Richardton chondrules, in the sense that they have been subjected to significantly less metamorphism than ordinary chondrules, and since the absolute RE abundances in Mokoia and Chainpur chondrules are equal to or greater than those found in the respective whole chondrites, the overall RE decrease in Forest City and Richardton chondrules seems consistent with diffusion of REE out of the chondrules during metamorphism.

Since the Sc^{+3} and Lu^{+3} radii are rather similar at 0.81\AA and 0.85\AA , respectively, the element Sc, which has some chemical

properties similar to the REE and particularly to the heaviest RE, Lu, would be expected to diffuse out of chondrules less than Lu. It is implicitly assumed that the REE and Sc are occluded in the same chondrule mineral, although such may not be the case. It has been experimentally observed (Schmitt et al, 1967b) that the ratios of Sc in chondrules to the whole-rock chondrites was 1.19 ± 0.43 , 1.14 ± 0.42 , 1.90 ± 0.66 and 1.63 ± 0.62 for Mokoia, Chainpur, Forest City and Richardton, respectively. Values (\pm) cited above largely indicate the population standard deviation spread of Sc in ~ 20 individual chondrules determined for each chondrite. Other Sc chondrule abundances from the above investigations show a similar trend that chondrules from ordinary chondrites are richer in Sc compared to chondrules from Type III carbonaceous or unequilibrated chondrites. If any Sc diffusion has occurred during metamorphism, the Sc data suggests a diffusion net gain by the chondrules, which apparently is in an opposite direction to any RE diffusion,

The fact that abundances of Lu and Yb are $\approx 20\%$ less in chondrules compared to their matrices does not force the conclusion that RE abundances were originally identical in chondrules and in the whole-rock chondrites. Formation of chondrules at high temperatures may have been a sufficiently complicated process to accrete variable quantities of REE into chondrules and into the matrix material. However, at the inferred accretion temperatures for the formation of

the high temperature matter (fraction B of Larimer and Anders (1967) and chondrules of Wood (1963): $>1300^{\circ}\text{K}$ and $\sim 1200^{\circ}\text{K}$ for Type III carbonaceous and ordinary chondrites, respectively), the volatility properties of the REE and Sc are sufficiently varied to introduce some fractionation, but not in the observed pattern. Following the method and assumptions of Larimer and Anders (1967), we have calculated the condensation temperatures for a few critical REE (see Table 2). A total pressure of 1 and 6.6×10^{-3} atmospheres and normal cosmic elemental abundances of the elements were assumed and the most recent RE thermodynamic data by Research Chemicals (1966) was used in the calculations.

Table 2. Condensation Temperatures of Pure RE Metals

<u>Element</u>	<u>$P_T = 1 \text{ atm.}$ Temp. $^{\circ}\text{K}$</u>	<u>$P_T = 6.6 \times 10^{-3} \text{ atm.}$ Temp. $^{\circ}\text{K}$</u>
57La	1300	1150
58Ce	1360	1200
59Pr	1120	980
62Sm	560	480
63Eu	550	490
70Yb	590	520
71Lu	1250	1120
21Sc	1250	1090

The fast cooling mechanism for condensation of the pure REE can be ruled out insofar as chondrule formation is associated with the inferred high temperatures. At an inferred $>1300^{\circ}\text{K}$ temperature for chondrule formation in Type III carbonaceous chondrites, Sm, Eu and Yb would have been severely fractionated with respect to La, Ce, Lu and Sc for total pressures of 6.6×10^{-3} or 1 atmosphere, both of which are well within the predicted range of pressures. In addition, the observed smooth linear fractionation of the REE in chondrules from ordinary chondrites rules out condensation of pure RE metals at $\sim 1200^{\circ}\text{K}$. Moreover, the observed fractionation is in the opposite direction to prediction; i.e., Sm, Eu, Yb and Lu according to this pure-metal fast cooling condensation mechanism would have been progressively depleted in chondrules and the reverse is observed. In addition, there is no significant fractionation between the adjacent REE, Yb and Lu, with their large condensation difference of $\sim 600^{\circ}\text{K}$.

In the above discussion, it has been assumed that the RE distribution in the matrix (Wood 1963) or fraction A matter of Anders (1964) represent the primordial distribution. Fraction-A matter for Type III carbonaceous and ordinary chondrites presumably accreted at temperatures of $\leq 400^{\circ}$ and $530\text{--}650^{\circ}\text{K}$ (Larimer and Anders 1967). No significant RE fractionation would be anticipated at these temperatures, even for the metal condensation mechanism. It is highly probable that RE oxides and silicates were formed at high temperatures

of $>1000^{\circ}\text{K}$ and were more involved in the condensation history than the pure metals. Thermodynamic data of the RE oxides and silicates are needed to decide whether the observed RE fractionation in chondrules from ordinary chondrites occurred during or subsequent to accretion of chondrules.

Vaporization data of some RE oxides at elevated temperatures by White *et al.* (1962) show that the volatilities of the RE sesquioxides decrease markedly with atomic number. For example, at 2500°K , rates of effusion of La_2O_3 , Nd_2O_3 , Sm_2O_3 , Gd_2O_3 and Y_2O_3 from a tungsten Knudsen cell were 13, 7.0, 4.7, 1.6 and $0.25 \times 10^{-4} \text{ gm cm}^{-2} \text{ sec}^{-1}$, respectively. At 2550°K , the effusion rate of Lu_2O_3 , the last REE, is approximately 0.1 of the Gd_2O_3 rate. Since the partial pressure of a gaseous species is directly proportional to the effusion rate and only inversely as the square root of the molecular weight, the partial pressure of the REE will be almost directly related to the effusion rate. For equal abundances of the REE in a solar nebula—e.g., La, Sm and Gd, are within a factor of two of each other—the heavy RE oxides will condense before the light RE oxides, which is in line with the observed fractionation pattern in chondrules from ordinary chondrites. Thermodynamic calculations on RE oxides in equilibrium with abundances of H_2 , O_2 and H_2O in the primeval solar nebula should be carried out on a quantitative basis in order to establish their precise condensation temperatures.

The nearly identical abundances of Eu in the chondrules and whole-rock chondrites of Forest City and Richardton (Fig. 2) strongly suggest that the preponderance of Eu exists or existed in the divalent oxidation state in chondrules and the chondritic matrix during metamorphism. If Eu diffusion has occurred, equilibration has been reached, resulting in zero net transport for Eu across the chondrule surface. Other divalent cations such as Fe, Mg and Mn have been equilibrated between the chondrules and matrices (Mason 1963, Keil and Fredriksson 1964, and Schmitt et al. 1965 and 1967b).

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Element	Radionuclide ^a	Mokoia ^b		Chainpur ^c		Forest City ^d		Richardton ^e		Average Normalized Abundances in 20 Chondrites ^f
		Absolute		Absolute		Absolute		Absolute		
		Normalized	Normalized	Normalized	Normalized	Normalized	Normalized	Normalized	Normalized	
La	La ¹⁴⁰	0.60±0.03	1.33	0.29±0.02	1.53	0.13±0.01	0.78	0.14±0.01	0.93	1.72±0.17
Ce	Ce ¹⁴³	1.64±0.18	3.64	0.84±0.08	4.42	0.48±0.08	2.88	0.49±0.07	3.27	5.02±0.40
Pr	Pr ¹⁴²	0.30±0.02	0.67	0.14±0.01	0.74	0.079±0.004	0.47	0.071±0.005	0.47	0.70±0.11
Nd	Nd ¹⁴⁷	--	--	--	--	--	--	--	--	3.32±0.34
Sm	Sm ¹⁵³	0.44±0.01	0.98	0.191±0.006	1.00	0.141±0.003	0.84	0.124±0.003	0.83	1.17±0.09
Eu	Eu ^{152m}	0.158±0.004	0.35	0.061±0.001	0.32	0.089±0.002	0.53	0.082±0.002	0.55	0.43±0.05
Gd	Gd ¹⁵⁹	0.52±0.10	1.16	0.28±0.07	1.47	0.29±0.04	1.74	0.22±0.04	1.47	1.84±0.22
Tb	Tb ¹⁶⁰	--	--	--	--	--	--	--	--	0.29±0.04
Dy	Dy ¹⁶⁵	0.75±0.05	1.67	0.34±0.02	1.79	0.23±0.03	1.38	0.22±0.02	1.47	1.75±0.20
Ho	Ho ¹⁶⁶	0.145±0.006	0.32	0.068±0.004	0.36	0.052±0.002	0.31	0.054±0.004	0.36	0.42±0.05
Er	Er ¹⁷¹	0.50±0.06	1.11	0.22±0.03	1.16	0.17±0.02	1.02	0.16±0.02	1.07	1.23±0.15
Tm	Tm ¹⁷⁰	0.073±0.005	0.16	0.036±0.004	0.19	0.029±0.005	0.17	0.029±0.003	0.19	0.18±0.02
Yb	Yb ¹⁷⁵	0.45±0.02	1.00	0.19 ±0.01	1.00	0.167±0.005	1.00	0.150±0.006	1.00	1.00
Lu	Lu ¹⁷⁷	0.069±0.004	0.154	0.030±0.004	0.16	0.026±0.003	0.16	0.025±0.003	0.19	0.18±0.02
Y	Y ⁹⁰	5.7±0.6	12.7	2.6±0.3	13.7	1.8±0.2	10.8	1.5±0.2	10.0	11.5±1.2
REE ^g		12.5		5.9		4.1		3.7		
Lu/Eu ^h		2.8±0.1		3.1±0.1		1.6±0.1		1.5±0.1		2.7±0.4

^a The nuclides Sm¹⁵³ and Eu^{152m} were measured by γ -ray scintillation spectroscopy and La¹⁴⁰ by both beta counting and scintillation spectroscopy. All other nuclides counted by Sharp Lowbeta counter (≈ 0.3 cpm background). The data reported in this table was first given by Schmitt and Smith (1965).

^b Thirty magnetic Mokoia chondrules, 0.079 g total, were analyzed in toto.

^c Thirty nonmagnetic Chainpur chondrules, 0.080 g, were analyzed.

^d Thirty-five nonmagnetic Forest City chondrules, 0.081 g, were analyzed.

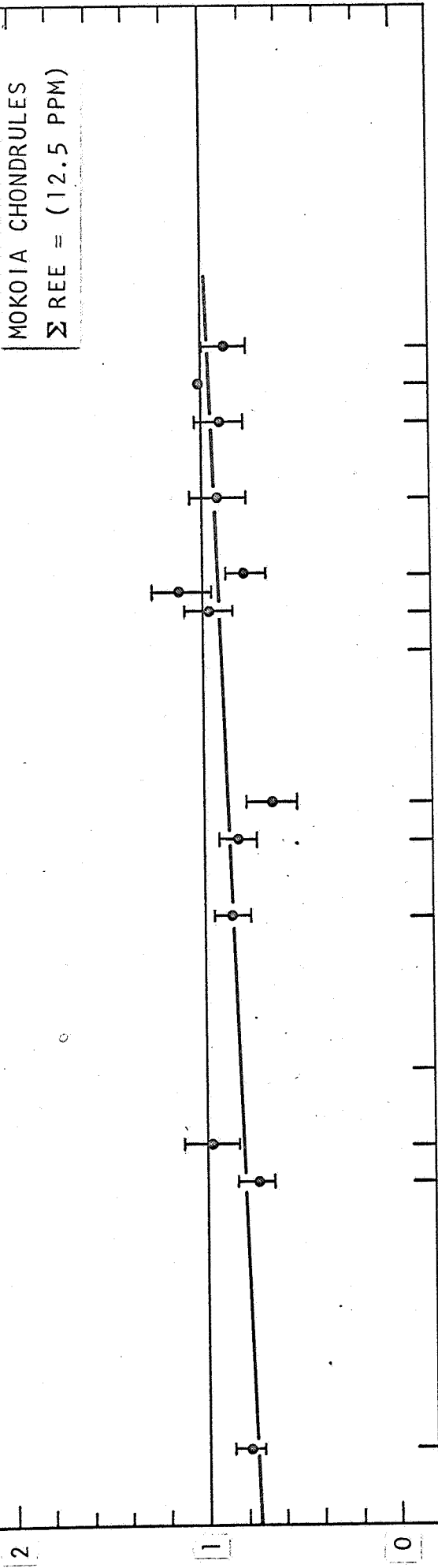
^e Fifty nonmagnetic Richardton chondrules, 0.077g were analyzed.

^f Taken from Table 5 of Haskin, et. al., (1966).

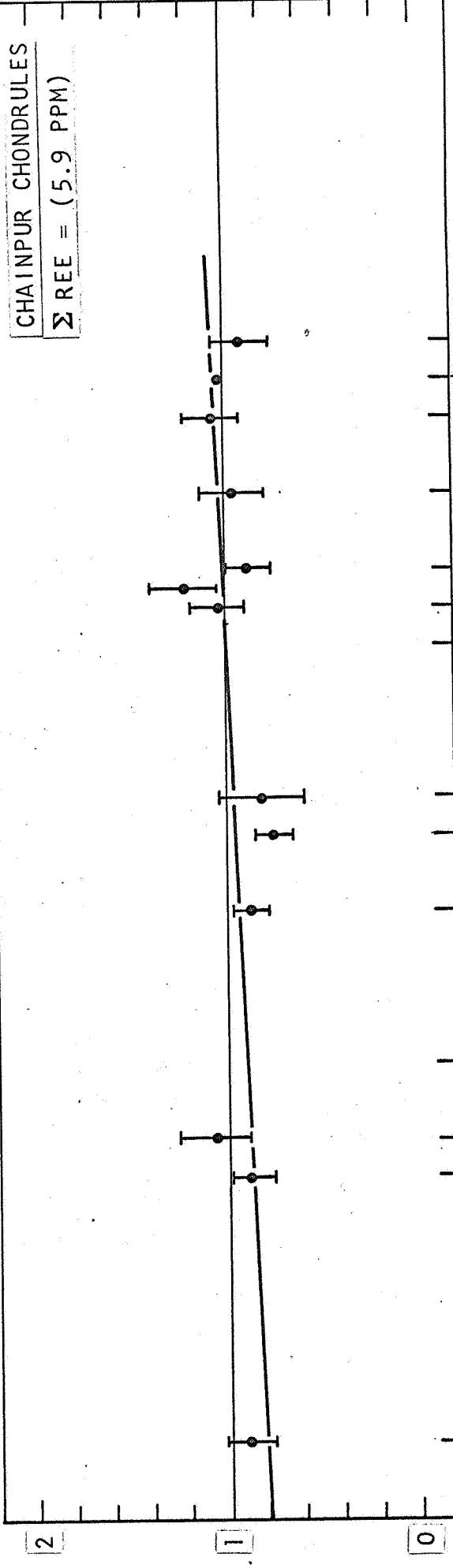
^g Abundance of the 14 REE plus Y have been summed. Values for Nd and Tb have been interpolated.

^h Abundance of the 14 REE plus Y concentrations since both elements are determined

MOKOIA CHONDRULES
 Σ REE = (12.5 PPM)



CHAINPUR CHONDRULES
 Σ REE = (5.9 PPM)



RARE-EARTH IONIC RADII (Å)

La	1.14
Ce	1.07
Pr	1.06
Nd	1.04
Sm	1.00
Eu	0.98
Gd	0.97
Tb	0.93
Dy	0.92
Ho	0.91
Er	0.89
Tm	0.87
Lu	0.85
Yb	0.86

CHONDRULES/CHONDRITES