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Archean Metaterrigenous Rocks: Major Geochemical Constraints

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Abstract—The paper summarizes data on the geochemistry of metaterrigenous rocks from 26 reference Archean territories: the Pilbara and Yilgarn blocks; Isua and Akilia complexes; Wittwatersrand, Swaziland, Pongola, and Yellowknife supergroups; Khapchanskaya and Gimol'skaya groups; Kan, Sharyzhalgai, Chupa, Slyudyanka, and Onot complexes; etc. The general sets of data points and the calculated median values of the concentrations of trace elements and their ratios are compared to those of Archean and post-Archean shales. In Ce/Cr–Co/Hf, Eu/Eu*–Gd_N/Yb_N, Ce/Cr–Th/Sc, Th/Sc–Sc, Th–La, La/Sm–Sc/Th, Yb–Gd_N/Yb_N, Th/Sc–Cr, Ni–Cr, and some other diagrams, the fields in which the most data points of Archean metaterrigenous rocks group are outlined. The results of this research indicate that there are no values of geochemical parameters that are inherent only in Archean or only in post-Archean fine-grained terrigenous rocks. Within 80–85% confidence levels, most individual compositions of Archean metaterrigenous rocks are characterized by the following geochemical parameters: (1) Th/Sc < 0.6–0.7, (2) Ce/Cr < 0.6, and (3) Eu/Eu* > 0.70–0.75. If the median values are used, these ranges can be further constrained to (i) Th/Sc < 0.55, (ii) Ce/Cr < 0.4, (iii) Cr/Th > 25, and (iv) Th < 12 ppm. Compared to PAAS, Archean metaterrigenous rocks are characterized by higher median concentrations of Cr and Ni and the Eu/Eu*, Sc/Th, Cr/Th, and Co/Hf ratios, whereas the Nb, La, Ce, Yb, Hf, Th, and U concentrations and the La/Sm and Ce/Cr ratios of PAAS are, conversely, lower. The median values of the La_N/Yb_N ratios of reference Archean terranes can be either higher or lower than in PAAS, likely depending on the proportions of various rock types in the sources of the terrigenous material. The medians of the Gd_N/Yb_N ratios of ~60% of the reference Archean metaterrigenous terranes in our databank are slightly higher than the Gd_N/Yb_N ratios of PAAS. The median values of the La_N/Sm_N ratios of Archean terrigenous rocks are mostly slightly lower than the typical PAAS ratios.

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INTRODUCTION

The most general tendencies and relations in the accumulation of thick sedimentary sequences in the Late Precambrian in the northeastern and northern East European Platform are still not fully understood. No consensus was reached on even such issues as the position and composition of the sources of the terrigenous material [1–10 and others]. Analogous situations are typical of Late Precambrian sequences around the peripheries of the Siberian Platform.

Because of this, the principal problem formulated for the research conducted within the scope of the project "Precambrian Sedimentary Sequences in the Urals and Siberia: Types and Character of Provenances, Long-Term Variations in the Composition of the Crust, and the Recycling Problem" of the Ural and Siberian divisions of the Russian Academy of Sciences was formulated as the evaluation of the contributions of large basement fragments of various age and composition in the East European Platform (Volga–Ural, Central, and Kola) to the genesis of Vendian and Riphean sedimentary rocks in the eastern, northeastern, and northern peripheries of the platform. This task was planed to be fulfilled by analyzing the geochemistry of fine-grained terrigenous rocks contained in these sequences and by identifying the indicator characteristics typical of the erosion products of primitive (relatively immature) Archean sources.

However, there is still no consensus as to which geochemical criteria should be applied to subdivide these rocks (compare [11], [12], and others). Because of this, the aforementioned problem should involve the generalization of currently available literature data on the composition of Archean metaterrigenous rocks produced by the erosion of "primitive" protoliths in Archean greenstone belts and shelf zones.

Another reason for the utilization of literature data was the absence of adequate analytical materials on the Archean rocks in the Central and Volga–Ural segments of the East European Platform. The very first materials of this type were lately obtained on the Kola segment [13, 14, and others], although they are still of limited character.

In preparing the manuscript of this paper, we used analytical materials (more than 300 individual analyses)[1] on such geochemically thoroughly examined terranes as the Pilbara and Yilgarn blocks in West Australia; the Isua and Akilia complexes in western Greenland; crystalline schists from Montana, USA and Ontario, Canada; the Wittwatersrand, Swaziland, Pongola, and Yellowknife supergrous in South Africa and Canada; the Khapchanskaya Group in the Anabar Shield in northern central Siberia; the Kan and Sharyzhalgai complexes in the southwestern Siberian platform; the Chupa Complex of the Belomorian Mobile Belt; the Gimol'skaya Group in western Karelia; the Slyudyanka Complex [2] in the southwestern Baikal area; the Onot Complex in the southeastern Cis-Sayan area; and others [17–39, 13, 40, 41, 14, 42, 16, 43, and others].[2]

We intentionally did not group the analytical data into those typical of cratons and greenstone belts, because analogous rocks are contained in the Volga–Ural, Central, and Kola basement megablocks of the East European platform [44–48 and others] and provided terrigenous material for Riphean and Vendian sedimentary basins in its eastern, northeastern, and northern peripheries.

We also compared the general (for all of the aforementioned reference Archean territories) data-point sets and the calculated median values of some trace-element concentrations and ratios (Th, Sc, La, Ni, Cr, Yb, Gd_N/Yb_N, Eu/Eu*, La/Sm, Sc/Th, Co/Hf, Ce/Cr, and others; Table 1) with the compositions of Archean and post-Archean argillite: AS (Archean Shale) and PAAS (Post-Archean Australian Slate), respectively [11].[3] In the discriminant diagrams Ce/Cr–Co/Hf, Eu/Eu*–Gd_N/Yb_N, Ce/Cr–Th/Sc, Th/Sc–Sc, Th–La, La/Sm–Sc/Th, Yb–Gd_N/Yb_N, Th/Sc–Cr, Ni–Cr, and others, we provisionally outlined the fields encompassing most of the median data points of the Archean reference territories grouped.

The occurrence of the erosion products of primitive Archean sources in post-Archean sedimentary sequences also likely follows from the geochemical data obtained by Podkovyrov [51, 52, and others], who analyzed the origin of Late Precambrian rocks in the Uchur–Maya area in southern Yakutia (hypostratotypical stratigraphic section of the Riphean), data on the Cenozoic deposits of the Ceara Rise ~800 km south of the Amazon mouth [53], and some other materials (for example, [54]).

For example, Podkovyrov et al. [52] examined fine-grained terrigenous Riphean and Vendian rocks in the Uchur–Maya area of the Siberian Platform and determined that the shale of the Talyn Formation of the lowermost Middle Riphean contain erosion products of Early Proterozoic or older "primitive" protoliths, which had no pronounced Eu anomalies. Geochemically similar material was also identified in some other lithostratigrafic units of the Riphean.

Comparing the ratios of various trace elements (with one element of each ratio typical of Archean shales and the other of post-Archean fine-grained aluminosilicate clastic material), for example, Sc/Th, Dobson et al. [53] determined that the Cenozoic deposits in the Seara Rise recovered by an ODP borehole drilled comprise three geochemical groups of sediments. The first of these groups consisted of sediments with ages <13 Ma and enriched in Ce, Cs, Eu, La, Lu, Sm, Tb, Th, and Yb, i.e., elements typical of post-Archean shales. Conversely, the rocks with ages of 55–20 Ma in the vicinities of the Seara Rise are fine-grained terrigenous deposits notably depleted in elements typical of post-Archean shales (the erosion of Archean complexes is the most obvious from the low La and Th concentrations). Dobson et al. [53] believe that these compositional features of the fine-grained aluminosilicate clastic material of the Seara Rise were caused by changes in the position and composition of the terrigenous material due to tectonic events in the northern part of South America. The main sources of terrigenous material for the Amazon fan until the Middle Miocene are thought to be the Brazilian and Guyana shields, which were dominated by Archean rocks. Later tectonic processes modified the alimentation scheme of the Amazon, and this resulted in the predominance of the erosion products of the Phanerozoic complexes of the Andes in the Seara sediments.

GEOCHEMISTRY OF THE FINE-GRAINED TERRIGENOUS ARCHEAN ROCKS: A REVIEW

The distinguishing between Archean and post-Archean fine-grained terrigenous rocks was considered in detail in numerous papers by Taylor and McLennan published in the late 1970s–early 1990s [20, 55–57, 25,

[1] It is pertinent to mention that analytical materials presented by various researchers notably differ. Papers published by foreign geologists in the 1980s characterize reference Archean metaterrigenous associations by 7–10–12 individual analyses; not all REE are determined; and there are often no data on such trace elements as Nb, U, Hf, etc. Publications that appeared in the early 1990s commonly present more complete data (on a greater number of samples, which are analyzed for a greater number of elements). Papers in Russian published before the mid-1990s commonly present no data on the REE concentration of Archean metaterrigenous rocks. Although later publications did contain this information, it was still inadequately scarce. The situation was remarkably improved in the early 2000s (see, for example [13]).

[2] According to Kotov et al. [15], the Slyudyanka Complex was formed in its modern form in the Ordovician, but the principal geochemical features of the metaterrigenous gneisses of the Slyudyanka Complex notably differ from those of post-Archean schists and resemble those of ancient granulite–gneiss complexes and granite–greenstone terranes [16].

[3] As in our earlier publications, here we use the median values of the concentrations and ratios of certain elements, because these statistical parameters enabled us to give generalized assays for the analytical samplings with an unknown character of the distribution [49, 50].

26, 58, 59, 11, 60, and others].[4] For example, the high to very high concentrations of Ni, Cr, and V (as well as anomalously high Cr/V and Ni/Co ratios and low V/Ni) and the usual absence of negative Eu anomalies (Eu/Eu* ≈ 1.0) in mudstones and shales definitely suggests, according to these authors, erosion in the catchment areas of the Late Archean crust. At the same time, some Precambrian metasedimentary sequences are thought to have too high Cr and Ni concentrations compared to the contents that can be obtained by the erosion of any natural source (either of basic or ultrabasic composition). This seems to suggests that the sediments become somewhat enriched in Cr and Ni during weathering or transportation [24, 59, and others].

Also, Archean fine-grained terrigenous rocks are noted to have much lower concentrations of LREE than their post-Archean analogues, and the LREE/HREE ratios are 6–9 for the former and 8–12 for the latter [59, 11, 60, and others].

The REE patterns of Archean sedimentary rocks are much more variable than the patterns of post-Archean sedimentary rocks. The Archean sediments of the first cycle, which were produced by the destruction of tonalite–trondhjemite–granite (TTG) associations, are characterized by steep REE patterns notably depleted in HREE ($Gd_N/Yb_N > 2.0$), whereas the erosion products of rocks of more basic composition show more gently sloping REE patterns ($La_N/Yb_N \approx 6$–8, $Gd_N/Yb_N < 2.0$) [59, 11, 60, and others].

Conversely, the significant negative Eu anomalies of clayey rocks (≈ 0.65) testifies that the source rocks were formed at a significant contribution of crustal differentiation, as is most typical of the post-Archean evolutionary stage of the continental crust. Post-Archean fine-grained sedimentary rocks are also typically enriched in LREE and not depleted in HREE ($Gd_N/Yb_N < 2.0$) [11, 60, and others].

Since Archean granitoids, which are one of the principal sources of clastic material, are depleted in HREE relative to most post-Archean acid magmatic rocks, the La_N/Yb_N and Gd_N/Yb_N ratios of the fine-grained products of their erosion can also reflect the averaged age of rocks composing the ancient water catchment territories [61]. The differences between Archean and post-Archean acid rocks are clearly pronounced in the $(La/Yb)_N$–Yb diagram: Archean TTG series are characterized by high La_N/Yb_N ratios (from 5 to >150) and Yb varying from 0.3 to 8.5. Conversely, post-Archean magmatic rocks are characterized by low La_N/Yb_N ratios (<30) and Yb_N values from 4.5 to 20 [62, 63, and others]. However, the overlap of the fields of Archean and post-Archean compositions in this diagram is very significant.

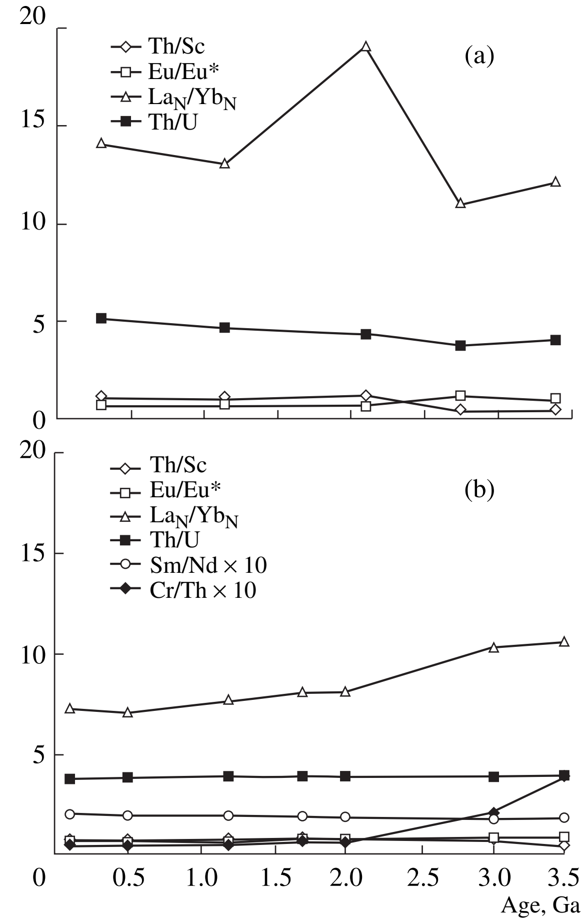


Fig. 1. Variations in the Th/Sc, Eu/Eu*, La_N/Yb_N, Th/U, Sm/Nd, and Cr/Th ratios in fine-grained terrigenous rocks over the past 3.5 Ga, according to (a) Taylor and McLennan and (b) Condie.

The Average Archean Shale has Th/Sc and La/Sc ratios of 0.43 and 1.3, respectively [11, 64] (Table 2). These ratios of the post-Archean rocks (as typified by PAAS) are equal to 0.91 and 2.7 (Fig. 1a). The Sc concentration in the Average Archean Shale is 19 ppm, and its Th and La concentrations are, respectively, 6.7 and 20 ppm.

The average value of the La/Th ratio is equal to 3.5 for fine-grained terrigenous Archean rocks and 2.7 for post-Archean sediments [59, 11].

The Th and U concentrations in Archean clayey rocks are, according to Taylor and McLennan, much lower (6.3 ppm Th and 1.6 ppm U) than in post-

[4] The evolution and character of ancient catchment areas are usually reconstructed using the proportions of certain trace elements (Cr, Ni, V, Th, Sc, and others) and REE in fine-grained aluminosilicate rocks, such as clays, mudstones, and shales. The elements listed above are characterized by very low solubilities in natural waters and, hence, are transported without any significant changes from ancient catchment areas to the final basins [59, 11, 60, 12, and others]. Sedimentation is coupled with weak REE fractionation, mostly because of the separation of heavy minerals, a process that does not play any significant role for clayey rocks. It is thus reasonable to assume that the fine-grained fraction of sedimentary rocks reflects the composition of the source. Diagenetic and metamorphic processes usually do not affect the REE distribution.

Table 1. Median concentrations (ppm) of some trace elements and their ratios in metaterrigenous rocks from some reference Archean terranes

Element or ratio	Pilbara	Isua	Montana	Wittwatersrand	Pontiac	Kalgoorlie	Yellowknife	Limpopo	Pongola
Sc	18.0 ± 3.8	19.0 ± 9.7	17.6 ± 15.1	24.0 ± 8.5	16.0 ± 13.1	–	17.0 ± 5.6	23.0 ± 11.8	12.5 ± 8.1
V	160.5 ± 54.3	87.0 ± 88.7	–	–	–	–	134.0 ± 42.2	148.0 ± 74.0	119.0 ± 63.3
Cr	619.5 ± 161.8	315.0 ± 154.9	346.0 ± 70.5	724.0 ± 318.8	158.0 ± 64.9	–	160.5 ± 39.9	255.0 ± 146.0	295.0 ± 200.4
Co	30 ± 10.2	30.0 ± 14.0	24.0 ± 26.1	43.0 ± 25.8	24.0 ± 5.6	–	–	26.00 ± 13.3	13.5 ± 7.5
Ni	337.5 ± 150.1	207.0 ± 75.0	122.0 ± 54.1	365.0 ± 149.5	65.0 ± 26.6	–	70.0 ± 19.31	10.0 ± 76.0	85.5 ± 81.3
Nb	–	–	–	–	–	–	7.0 ± 1.4	11.0 ± 12.7	17.1 ± 4.1
La	34.9 ± 12.5	12.0 ± 9.6	31.6 ± 5.5	23.5 ± 19.9	29.9 ± 7.3	19.0 ± 8.8	25.6 ± 8.8	29.2 ± 9.9	28.3 ± 15.5
Ce	72.0 ± 26.3	22.0 ± 20.7	57.5 ± 11.9	49.5 ± 37.6	61.8 ± 19.1	40.0 ± 18.7	52.5 ± 16.7	50.6 ± 17.6	51.0 ± 25.2
Sm	5.8 ± 2.4	3.0 ± 1.4	4.3 ± 1.2	4.7 ± 2.9	4.8 ± 3.4	2.8 ± 1.2	4.6 ± 1.3	6.0 ± 1.7	4.3 ± 2.3
Yb	2.4 ± 0.9	2.3 ± 0.8	2.0 ± 0.8	2.2 ± 1.3	1.6 ± 0.4	1.3 ± 0.8	1.5 ± 0.4	3.0 ± 5.4	2.5 ± 1.4
Hf	4.8 ± 1.0	3.3 ± 1.4	–	3.9 ± 1.9	3.3 ± 0.6	2.9 ± 0.9	3.5 ± 0.5	4.0 ± 1.0	4.3 ± 2.6
Th	11.1 ± 5.1	0.8 ± 1.9	10.5 ± 3.4	4.5 ± 3.4	6.7 ± 1.4	5.2 ± 4.4	6.9 ± 3.3	9.15 ± 5.1	7.7 ± 4.0
U	–	–	–	–	–	–	1.5 ± 0.5	1.6 ± 0.4	2.2 ± 1.3
La_N/Sm_N	3.7 ± 0.3	2.3 ± 1.2	4.3 ± 0.6	3.5 ± 0.5	3.9 ± 0.9	4.3 ± 1.1	3.6 ± 0.6	3.6 ± 1.2	3.9 ± 1.2
La_N/Yb_N	8.8 ± 1.7	4.1 ± 6.8	10.3 ± 2.7	7.4 ± 2.0	12.7 ± 0.1	6.2 ± 20.5	12.0 ± 4.7	7.8 ± 4.8	8.1 ± 9.8
Gd_N/Yb_N	1.4 ± 0.1	1.2 ± 0.6	–	–	–	1.4 ± 2.3	1.9 ± 0.6	1.5 ± 0.6	1.2 ± 0.3
Eu/Eu*	0.89 ± 0.06	1.04 ± 0.20	–	–	–	1.12 ± 0.17	0.94 ± 0.17	0.65 ± 0.23	0.78 ± 0.05
La/Sm	5.9 ± 0.5	2.2 ± 2.0	6.7 ± 0.7	5.6 ± 0.8	6.1 ± 1.4	–	5.7 ± 0.7	5.8 ± 2.0	6.6 ± 1.9
Sc/Th	1.9 ± 0.6	25.3 ± 55.6	2.2 ± 0.8	3.8 ± 1.7	2.2 ± 3.5	–	2.5 ± 0.8	1.6 ± 11.7	2.0 ± 0.9
Co/Hf	5.9 ± 3.5	15.2 ± 15.9	–	11.9 ± 6.3	6.5 ± 3.2	–	6.7 ± 1.7	5.3 ± 7.2	4.1 ± 2.5
Ce/Cr	0.12 ± 0.06	0.02 ± 0.37	0.15 ± 0.04	0.07 ± 0.06	0.36 ± 0.79	–	0.35 ± 0.11	0.22 ± 0.07	0.21 ± 0.10
Th/Sc	0.52 ± 0.31	0.04 ± 0.15	0.45 ± 0.25	0.26 ± 0.12	0.46 ± 0.21	–	0.40 ± 0.22	0.6 ± 0.4	0.51 ± 0.15
n	12	11	7	24	3	7	28	5	17
Element or ratio	Fig Tree	Moodies	Khapchan-skaya	Kan	Sharyzhalgai	Chupa	Kapuskasing	Western Gneiss Terrane	Belingwe
Sc	21.5 ± 8.8	15.0 ± 1.5	16.0 ± 10.1	19.5 ± 10.5	40.5 ± 14.7	–	–	7.8 ± 16.4	43.0 ± 11.5
V	144.5 ± 74.7	100.0 ± 22.0	101.0 ± 69.2	126.0 ± 47.8	131.5 ± 63.8	123.0 ± 6.3	130.0	27.0 ± 139.1	302.0 ± 74.1
Cr	964.0 ± 479.3	679.0 ± 118.9	100.0 ± 52.3	100.0 ± 25.0	146.0 ± 75.7	226.0 ± 71.4	172.0	68.0 ± 302.7	464.0 ± 554.8
Co	46.0 ± 8.5	36.0 ± 3.3	12.5 ± 7.7	20.0 ± 9.6	23.0 ± 8.6	26.0 ± 1.9	–	36.0 ± 33.9	55.0 ± 19.1
Ni	509.0 ± 272.0	323.0 ± 47.8	16.0 ± 14.3	53.0 ± 21.7	55.0 ± 36.4	75.5 ± 33.1	69.0	31.0 ± 111.0	160.0 ± 158.1
Nb	8.9 ± 4.2	10.7 ± 1.6	13.5 ± 7.5	9.0 ± 1.5	–	5.5 ± 1.7	7.5 ± 0.7	7.5 ± 0.9	5.0 ± 1.6
La	16.3 ± 7.3	18.4 ± 8.3	38.0 ± 28.0	54.1 ± 15.7	58.0 ± 2.8	25.0 ± 2.3	16.0 ± 15.9	17.3 ± 16.6	6.7 ± 2.4
Ce	32.0 ± 15.7	37.8 ± 16.8	79.0 ± 68.6	89.0 ± 25.4	93.0 ± 5.7	53.0 ± 6.0	32.5 ± 25.8	48.3 ± 39.2	15.7 ± 5.4
Sm	3.3 ± 1.3	3.0 ± 1.3	3.3 ± 6.9	8.4 ± 2.0	7.8 ± 0.2	4.7 ± 0.5	3.6 ± 1.6	2.9 ± 0.6	2.1 ± 0.7
Yb	2.0 ± 0.6	1.6 ± 0.4	1.7 ± 1.1	2.6 ± 1.1	3.9 ± 1.5	1.4 ± 0.1	1.6 ± 1.1	1.7 ± 0.3	–
Hf	2.6 ± 1.2	4.4 ± 1.0	–	5.7 ± 3.4	6.6 ± 0.3	–	4.1 ± 0.6	3.0 ± 0.9	–

Table 1. (Contd.)

Element or ratio	Fig Tree	Moodies	Khapchanskaya	Kan	Sharyzhalgai	Chupa	Kapuskasing	Western Gneiss Terrane	Belinguwe
Th	4.4 ± 1.7	6.2 ± 1.0	9.5 ± 8.7	19.2 ± 11.6	17.7 ± 2.2	–	2.7 ± 2.8	9.2 ± 6.6	2.3 ± 1.5
U	1.2 ± 0.5	1.9 ± 0.4	–	1.5 ± 1.1	2.1 ± 0.7	–	0.4 ± 0.2	1.9 ± 2.1	–
La_N/Sm_N	3.0 ± 0.4	3.8 ± 0.2	4.5 ± 2.9	4.0 ± 0.9	4.7 ± 0.4	3.0 ± 0.2	3.5 ± 1.0	3.5 ± 3.4	1.6 ± 0.5
La_N/Yb_N	5.5 ± 1.9	8.2 ± 1.6	7.6 ± 64.5	15.1 ± 6.2	11.1 ± 4.8	12.4 ± 1.91	0.7 ± 7.0	6.8 ± 7.8	–
Gd_N/Yb_N	1.2 ± 0.3	1.3 ± 0.1	–	2.1 ± 0.7	–	–	1.6 ± 0.3	1.0 ± 0.2	–
Eu/Eu*	0.88 ± 0.20	0.92 ± 0.02	–	0.70 ± 0.15	–	–	1.00 ± 0.24	0.55 ± 0.12	0.93 ± 0.15
La/Sm	5.0 ± 0.4	6.1 ± 0.3	4.2	6.1 ± 1.5	7.5 ± 0.6	4.7 ± 0.4	5.5 ± 1.6	5.49 ± 5.45	2.6 ± 0.8
Sc/Th	4.3 ± 1.2	2.5 ± 0.3	1.9	1.0 ± 0.6	1.9 ± 1.1	–	–	0.8 ± 5.9	20.5 ± 12.3
Co/Hf	13.4 ± 9.0	8.8 ± 2.0	–	3.1 ± 2.0	2.8 ± 1.0	–	–	–	–
Ce/Cr	0.05 ± 0.04	0.06 ± 0.01	0.7 ± 7.9	0.92 ± 0.12	1.1 ± 0.2	0.34 ± 0.10	0.4	0.6 ± 0.8	0.021 ± 0.020
Th/Sc	0.24 ± 0.07	0.39 ± 0.05	0.47 ± 0.08	0.99 ± 1.87	0.64 ± 0.37	–	–	1.2 ± 1.5	0.049 ± 0.036
n	7	5	17	11	4	4	3	3	15

Element or ratio	Gomol'skaya	Ontario	Slyudyanka	Onot	Kambalda	Abitibi	Kongling	Buhwa
Sc	19.0 ± 4.8	14.5 ± 12.5	35.5 ± 6.5	–	–	6.0 ± 5.8	16.0 ± 4.6	17.0 ± 7.3
V	118.0 ± 41.5	154.5 ± 55.9	238.5 ± 32.7	163.0 ± 47.9	75.5 ± 24.41	12.0 ± 28.4	86.0 ± 47.4	125.0 ± 45.4
Cr	187.0 ± 45.5	70.0 ± 88.1	342.5 ± 207.3	177.0 ± 83.0	114.0 ± 76.3	173.5 ± 220.7	177.0 ± 99.4	290.0 ± 755.4
Co	25.0 ± 6.1	32.5 ± 17.3	27.0 ± 8.7	26.0 ± 7.6	61.0 ± 39.2	22.0 ± 9.6	22.0 ± 8.6	14.0 ± 15.8
Ni	60.0 ± 21.2	55.5 ± 40.7	276.0 ± 180.7	120.0 ± 38.9	115.0 ± 896.5	66.5 ± 112.9	107.0 ± 38.5	91.5 ± 305.3
Nb	8.0 ± 1.2	8.1 ± 2.8	–	6.4 ± 0.7	3.3 ± 1.1	12.0 ± 5.3	10.0 ± 4.9	8.8 ± 2.5
La	20.0 ± 8.0	33.3 ± 14.6	29.5 ± 9.6	24.0 ± 4.4	10.2 ± 5.5	25.5 ± 14.7	38.2 ± 10.3	–
Ce	39.0 ± 9.7	79.5 ± 20.2	58.5 ± 21.2	50.0 ± 5.5	21.9 ± 10.6	52.0 ± 26.9	73.7 ± 19.6	24.9 ± 9.8
Sm	4.0 ± 0.9	6.3 ± 3.0	5.8 ± 2.7	4.8 ± 0.7	2.7 ± 1.0	4.0 ± 1.7	5.3 ± 1.3	2.6 ± 1.1
Yb	1.2 ± 0.3	1.5 ± 0.4	3.2 ± 1.1	1.9 ± 0.4	1.5 ± 0.8	1.3 ± 0.3	2.5 ± 0.8	1.7 ± 0.5
Hf	3.1 ± 0.3	3.6 ± 1.0	–	3.2 ± 0.3	2.8 ± 1.1	3.0 ± 0.7	4.9 ± 0.8	–
Th	5.2 ± 0.9	3.2 ± 5.0	–	8.0 ± 1.1	–	4.6 ± 2.1	7.7 ± 3.4	13.0 ± 4.6
U	1.2 ± 0.3	0.8 ± 0.2	–	–	–	1.3 ± 1.5	2.3 ± 1.2	–
La_N/Sm_N	3.1 ± 1.0	4.0 ± 2.1	3.1 ± 0.4	3.1 ± 0.2	2.5 ± 0.7	4.0 ± 0.9	4.7 ± 0.7	–
La_N/Yb_N	8.7 ± 3.7	16.5 ± 4.0	6.7 ± 5.8	9.3 ± 2.1	4.3 ± 1.2	13.5 ± 11.5	11.8 ± 4.8	–
Gd_N/Yb_N	–	2.2 ± 0.7	1.6 ± 0.8	2.0 ± 0.2	1.3 ± 0.2	–	1.8 ± 0.4	1.3 ± 0.3
Eu/Eu*	–	0.94 ± 0.2	60.9 ± 0.2	0.76 ± 0.07	0.99 ± 0.31	0.92 ± 0.16	0.82 ± 0.21	0.76 ± 0.01
La/Sm	4.9 ± 1.6	6.3 ± 3.4	5.0 ± 0.7	5.0 ± 0.4	3.9 ± 1.0	6.3 ± 1.5	7.4 ± 1.1	–
Sc/Th	3.9 ± 0.6	3.5 ± 7.9	–	–	–	3.4 ± 7.5	1.9 ± 1.1	1.2 ± 5.4
Co/Hf	10.0 ± 2.2	9.1 ± 11.7	–	8.7 ± 2.7	31.4 ± 18.9	7.6 ± 5.5	5.1 ± 2.5	6.8 ± 2.1
Ce/Cr	0.24 ± 0.07	0.91 ± 0.61	0.17 ± 0.10	0.28 ± 1.30	0.19 ± 0.16	0.28 ± 0.25	0.34 ± 0.46	0.13 ± 0.08
Th/Sc	0.26 ± 0.06	0.33 ± 0.32	–	–	–	0.29 ± 0.17	0.5 ± 0.3	0.8 ± 0.4
n	39	4	12	5	16	34	14	14

Note: number of analyses used to calculate the median concentrations of trace elements and their ratios; dashes mean no data.

Table 2. Concentrations (ppm) of some trace elements and their ratios in the Average Archean Shale and PAAS (data from [11])

Element or ratio	Average Archean Shale	PAAS
Sc	19.0	16.0
V	135	150
Cr	~440	110
Co	40	23
Ni	~250	55
Nb	9	19
La	20.0	38.0
Ce	42	80
Sm	4	5.6
Yb	2	2.8
Hf	3.5	5
Th	6.3	14.6
U	1.6	3.1
La_N/Sm_N	3.15	4.27
La_N/Yb_N	6.8	9.2
Gd_N/Yb_N	1.38	1.36
Eu/Eu*	~1.0	0.66
La/Sm	~5.0	6.78
Sc/Th	3.17	1.1
La/Sc	1.3	2.7
Co/Hf	11.43	4.6
Ce/Cr	0.1	0.73
Th/Sc	0.43	0.91

Archean rocks (14.6 ppm Th and 3.1 ppm U). The Th/U ratio of Archean shales broadly varies and averages 3.9, which is lower than that of the post-Archean rocks (4.5–5.5) [59].

The aforementioned researchers believe that data on the concentrations of incompatible and compatible elements, including Th, Sc, and La and the Th/Sc, La/Sc, Eu/Eu*, and LREE/HREE ratios in terrigenous fine-grained rocks testify that the concentrations of these elements in the upper crust did not change any significantly in post-Archean time.[5]

At the same time, several geologists [29, 65, 12, 66, 67, and others] believe that these data were obtained by comparing sediments that had various ages and were formed in various tectonic environments; hence, the compositional variations of the continental crust at the Archean–Proterozoic boundary were most probably caused by the not fully accurate comparison of tectonically diverse rocks (from greenstone belts and cratons) of various age.

According to Condie [65], Archean cratonic schists are characterized by elevated concentrations of Cr, Co, Ni, Mg, and Sc at lower concentrations of K, Rb, Ba, Pb, Th, U, Ca, Na, and Sr compared to post-Archean deposits. The former are also characterized by lower Th/U, Th/Sc, and La/Sc and higher Cr/Th, Co/Th, Co/Sc, and Ni/Co ratios.

The REE patterns of Archean schists are closely similar to the patterns of post-Archean rocks. The absence of an REE deficit in Archean terrigenous rocks is likely caused by the significant contribution of basalt–komatiite and tonalite associations to sedimentation processes.

According to Condie [65, 12], the terminal Archean was marked by a slight increase in LILE, P, Nb, Ta, Zr, and Hf concentrations in the upper continental crust. The same period of time was characterized by an increase in the Rb/Sr and Ba/Sr ratios. In contrast to Taylor and McLennan, Condie does not think that the Archean–Proterozoic boundary was marked by any significant changes in the Th/Sc ratio. The Th/U ratio also remained almost unchanging (and equal to ~3.7–3.9) throughout the whole Archean, Proterozoic, and Phanerozoic (Fig. 1b). According to Condie, the terminal Archean was marked only by a strong decrease in the REE fractionation and a slight increase in the Sm/Nd ratio.[6]

Condie also believes that the occurrence of a negative Eu anomaly only in post-Archean deposits that was postulated in all the publications by Taylor and McLennan is explained as stemming from the comparison of the predominantly Archean rocks of greenstone belts with post-Archean cratonic rocks. According to Condie, Archean schists and the Archean upper crust are characterized by notable negative Eu anomalies, which only slightly increased toward the end of the Archean. Condie also thinks [12] that this is explained by the fact that post-Archean TTG associations were characterized, in contrast to their Archean analogues, by significant negative Eu anomalies. The analysis of data on cratonic schists alone indicates that the height of Eu anomalies in the post-Archean upper crust was only slightly greater than in the Archean.

In should, however, be mentioned that the discussion of Taylor and McLennan with Condie eventually resulted in a slight convergence of their opinions. For example, already in their paper devoted to high-grade metamorphic rocks in the Kapuskasing structural zone in Canada, Limpopo Belt in South Africa, and Western

[5] It is, however, necessary to stress that this conclusion is based on limited material (no more than 48 analyses [11]) on post-Archean rocks from Australia, New Zealand, and Antarctica.

[6] Condie emphasized that the trends that he determined in the variations in the Lai_N/Yb_N and Sm/Nd ratios with time are opposite to the trends proposed by Taylor and McLennan [11].

Gneiss Terrane in Australia, Taylor et al. [58] stated that the granulite-facies metaterrigenous rocks of the Limpopo Belt and Western Gneiss Terrane show REE patterns typical of both post-Archean terrigenous deposits and Archean sedimentary rocks.[7] These authors believe that this is explained by local variations in the compositions of the eroded areas: the rocks with "post-Archean" REE patterns (which are characterized by, for example, negative Eu anomalies) were presumably formed of the erosion products of high-K granite plutons that composed small stable Early Archean areas. The appearance of these areas predated Late Archean–Proterozoic events accompanied by the extensive migmatization of the upper continental crust.

These researchers largely reached a consensus about the predominance of rocks with elevated Ni, Co, and Cr concentrations in the Archean upper crust and fine-grained terrigenous cratonic sediments and about their high Cr/Th, Co/Th, and Ni/Co ratios. The likely reason for the decrease in the overall Ni, Co, and Cr concentrations and in these ratios in post-Archean rocks was the overall decrease in the amount of high-Mg basalts and komatiites in the continental crust. This tendency is most clearly pronounced in the Early Precambrian rocks of the Kaapvaal craton [61, 12].

According to Eriksson et al. [68], the evolution of the sedimentary filling of Early Precambrian basins was controlled, first of all, by magmatic processes, but it is still unclear whether these processes were related to plate tectonic processes. The sedimentary–volcanic sequences of Archean greenstone belts were formed in diverse tectonic environments, including mid-oceanic ridges (?), island arcs, and oceanic plateaus, i.e., all of the structures characterized by high heat flows. Deposits younger than 2.0 Ga contain practically no such rocks, although some researchers do not agree with this opinion. Active Early Archean magmatism resulted in the development of protocratons, whose rocks were extensively weathered in fairly aggressive environments. The Late Archean rocks of several large basins (for example, Wittwatersrand, 3074–2714 Ma) are quite close to the deposits of greenstone belts but differ from them in sedimentation that occurred in more stable environments and was controlled by the eustatic variations in the sea level and climate, which facilitated the appearance of somewhat more mature sedimentary associations.

RESULTS AND DISCUSSION

This section presents a concise summary of our earlier results obtained by the analysis of literature data on the geochemistry of metaterrigenous rocks (predominantly clayey ones) of 26 reference Archean terranes.

[7] The Kapuskasing structural zone is a deeply eroded greenstone belt, whereas the Limpopo belt and Western Gneiss Terrane are dominated by shelf metaterrigenous sequences on a granite basement.

The Sc concentrations in Archean metaterrigenous rocks vary from 2 to 40 ppm (Fig. 2a), but the overwhelming majority of samples of fine-grained aluminosilicate clastic rocks of this age interval are characterized by Sc concentrations within the range of 10–30 ppm, which significantly overlaps with the Sc concentrations in such geochemical reference rocks as Average Archean Shale (19 ppm) and PAAS (16 ppm) [11].

The median Sc concentrations in the great majority of reference Archean terranes (>90%) vary from 12 to 25 ppm (Fig. 3a), and only the granulites of the Sharyzhalgai Complex have much higher median Sc contents (~40 ppm). This provides sound reasons to believe that the terrigenous rocks of the Sharyzhalgai Complex were formed of material eroded in source areas dominated by basic and ultrabasic rocks. However, according to Nozhkin and Turkina [35], the high Th and REE concentrations of the Sharyzhalgai granulites suggest that their ancient catchment areas were dominated by rocks of diorite–granodiorite composition, comparable with Ca-granitoids of composition close to that of the early sialic crust.

The median V concentration in Archean metaterrigenous rocks is equal to 122 ppm, but the scatter of the values is as significant as two orders of magnitude, from 3 to 398 ppm. The highest V concentrations are typical of metasedimentary rocks of the Belingwe greenstone belt in Zimbabwe, South Africa, which were composed of the erosion products of predominantly basic volcanics [43].

Danchin [69] seems to be the first to note high Cr and Ni concentrations in Archean metaterrigenous rocks. Indeed, the Cr concentrations of Archean metaterrigenous rocks generally range from 10 to 1500–1700 ppm (Fig. 2b), with the overwhelming majority of the samples in our databank having Cr concentrations higher than 80–90 ppm. They can be subdivided into two groups: (i) with 100–350 ppm Cr and (ii) with >350–400 ppm Cr. It is worth mentioning that the Cr concentration of PAAS (110 ppm) is slightly higher than the lower limit of the first group, and the average Cr concentration in the Average Archean Shale (~440 ppm) is only slightly higher than the lower limit for the samples of the second group.[8]

The median Cr concentrations calculated for 20 reference Archean terranes of the overall databank are also mostly (~80%) intermediate between the concentrations in the Average Archean Shale and PAAS, and only the metaterrigenous rocks of the Pilbara block (~3.4 Ga), Moodies (~3.4 Ga) and Fig Tree (>3.4–3.5 Ga) groups, and the Wittwatersrand Supergroup (~2.7 Ga) have higher Cr concentrations than those of the Average Archean Shale (Fig. 3b), which is typical, according to Taylor and McLennan [11], of Early Archean sedimentary rocks.

[8] As the Ni, V, and Co concentrations discussed below, this value is an arithmetic mean of the Cr concentrations in Early and Late Archean shales [11].

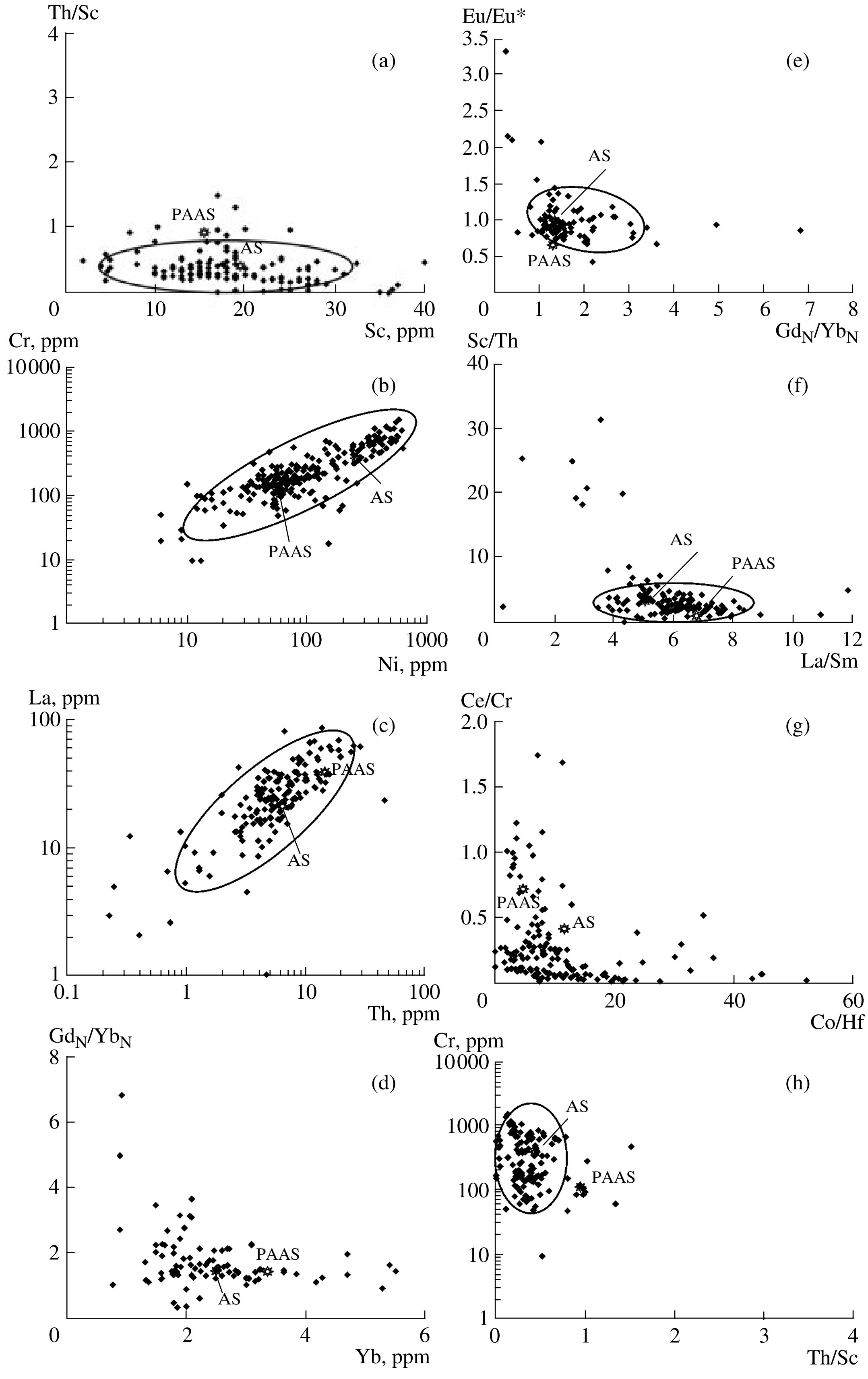


Fig. 2. Various geochemical diagrams showing the compositions of individual samples of Archean metaterrigenous rocks. *AS*—Average Archean Shale; PAAS—Post-Archean Australian Shale [11]. Ellipses show the highest concentrations of data points.

The median Co concentration in Archean metaterrigenous rocks in our databank is 25.0 ± 21.2 ppm (the maximum and minimum values are 131 and 4 ppm, respectively). The Co concentration of the Average Archean Shale is 40 ppm [11].

The concentrations of both Ni and Cr significantly vary. The overall scatter in the Ni concentration in the Archean fine-grained terrigenous rocks included in our databank is more than two orders of magnitude, from 5–6 to 700 ppm, with the range of 200–700 ppm represented by a number of samples only insignificantly lower than that for the range of 30–150 ppm (Fig. 2b). The Ni concentration in the Average Archean Shale (~250 ppm) corresponds to the former range, and that of PAAS is close to 55 ppm, i.e., a value lying within the latter range. This implies that only rocks with much higher Ni and Cr concentrations than those in PAAS can be considered as produced by the erosion of primitive Archean sources.

The median Ni concentration in the metaterrigenous rocks of the Kan and Chupa complexes, Abitibi and Ontario greenstone belts, Gimol'skaya Group, and the Yellowknife and Pongola supergroups roughly correspond to the Ni concentration in PAAS or are insignificantly higher (Fig. 3b). An Ni concentration intermediate between those in PAAS and the Average Archean Shale are characteristic of the crystalline schists from Montana, the Isua association, the Onot Complex, and the Kambalda Group in the Yilgarn block in western Australia. Finally, a very low median Ni concentration of 15–17 ppm (recall that the Ni concentration in PAAS is 55 ppm) was determined in paragneisses of the Khapchan Group of the Anabar Shield.

The La concentrations are generally scattered from 2 to 90 ppm (Fig. 2c), but the great majority of samples of fine-grained Archean rocks in our data bank have La concentrations within 10–70 ppm. However, even this narrower range includes La contents typical of the Average Archean Shale (20 ppm) and PAAS (38 ppm). Similar median La concentrations were also determined for reference Archean terranes: approximately 60% of them show La concentrations intermediate between those in PAAS and the Average Archean Shale (Fig. 3c). The rocks of the Isua association and the Fig Tree and Moodies groups contain less La than in the Average Archean Shale, and the granulites of the Kan and Sharyzhalgai complexes have median La concentrations higher than in PAAS.

Similarly to most of the elements considered above, Yb shows a significant scatter of its concentrations: from 0.2–0.3 to 5 ppm (Fig. 2d). This range includes the Yb concentrations of the Average Archean Shale (2.0 ppm) and PAAS (2.8 ppm). Most samples of Archean metaterrigenous rocks show Yb concentrations within the range of 1–2.5 ppm and are thus somewhat different from post-Archean terrigenous rocks. At the same time, the median Yb concentration in the Slyudyanka Complex is higher than in PAAS. The metaterrigenous Archean rocks of the Kan Complex, Isua association, Pilbara block, and the Pongola Supergroup have Yb concentrations intermediate between those in PAAS and the Average Archean Shale. The Yb concentrations of the rest of the reference territories are comparable with those typical of the Average Archean Shale or are lower (Fig. 3d).

The lowest Th concentrations in Archean fine-grained terrigenous rocks are ~0.25 ppm and the highest values are 45–50 ppm (Fig. 2c). The overwhelming majority of samples in our databank have Th concentrations from 3 to 10–10.5 ppm. This range also includes the values typical of the Average Archean Shale (6.7 ppm), whereas the Th concentration in PAAS is notably higher (14.6 ppm). This seems to enable the provisional approximate discrimination between Archean and post-Archean sources.

Median Th concentrations higher than those in PAAS were determined only in the rocks of the Sharyzhalgai and Kan complexes, and all the other reference terranes (~90%) in our databank have Th concentrations lower than that of PAAS.

The Gd_N/Yb_N ratio in Archean fine-grained terrigenous rocks varies from 0.2–0.3 to 6.8 with most of the samples characterized by ratios from 1 to 1.8 (Fig. 2e), which implies the absence of any significant depletion in HREE in most Archean metaterrigenous rocks. Only approximately 7–10% of the samples of our databank show $Gd_N/Yb_N > 2$. It is worth noting that the Gd_N/Yb_N ratio of the Average Archean Shale (1.38) is practically identical to that of PAAS (1.36 ppm).

The comparison of the median values of the Gd_N/Yb_N ratio of metaterrigenous rocks from various reference Archean terranes led us to conclude that only some of them (the Yellowknife Supergroup and the Kan and Onot complexes) display this ratio suggesting HREE depletion ($Gd_N/Yb_N > 2.0$) (Fig. 3e).

The scatter in the Eu/Eu* ratios of individual samples of Archean terrigenous rocks is 0.45–2.2 but the great majority of the samples in our databank are characterized by Eu/Eu* ratios from 0.75–0.8 to 1.0–1.1; i.e., the negative Eu anomaly in Archean sedimentary rocks is slightly lower than in post-Archean shales and mudstones but not as lower as was anticipated by Taylor and McLennan [11]. Recall that these authors believe that the Average Archean Shale has no negative Eu anomaly, and this anomaly in PAAS is only 0.66. Thus, available analytical data on a significant selection of Archean metaterrigenous rocks indicate that the overwhelming majority of these rocks are characterized by Eu/Eu* ratios intermediate between those in PAAS and the Average Archean Shale.

The median values of Eu anomalies in rocks from all of the reference Archean terranes in our databank are lower than those typical of PAAS (only the granulites from the Kan and Onot complexes are characterized by Eu/Eu* ratios of 0.70 ± 0.15 and 0.76 ± 0.07, respectively; Fig. 3e). In our opinion, these data suggest that only post-Archean fine-grained terrigenous rocks with Eu/Eu* ratios lower than 0.75 can be regarded as containing much of the erosion products of primitive Archean sources.

The La/Sm ratios of the majority of the samples of Archean terrigenous rocks varies from 4 to 8, with the lowest values of ~0.3 and the highest ones of 11.95–12.0 (Fig. 2f). Inasmuch as this ratio is equal to 5 for the Average Archean Shale and 6.78 for PAAS [11], the data presented above indicate that the La/Sm ratio does not make it possible to differentiate between Archean and post-Archean aluminosilicate clastic rocks.

Approximately 80% of the reference Archean terranes have median La/Sm ratios ranging from those of PAAS and the Average Archean Shale (Fig. 3f). The median La/Sm ratio in the granulites of the Sharyzhalgai Complex is higher than in PAAS, and the median ratios of the Khapchan Group of the Anabar Shield and the Isua association are notably lower than in the Average Archean Shale.

The Sc/Th ratio of Archean fine-grained terrigenous rocks ranges from <0.5 to 32, but the vast majority of the values lie within the range of 2–6 (Fig. 2f). This range also includes the values of the Average Archean Shale (3.17) and PAAS (1.1). However, with regard for the fact that the Sc/Th ratio of PAAS is remarkably lower than in most Archean terrigenous rocks, it can be suggested that relatively high values of this ratio (>2 or 2.5) definitely testify to the erosion of terranes composed of primitive Archean source material. This also follows from the fact that most of the Archean reference terranes (90–95%) have median Sc/Th ratios higher than that of PAAS (1.1), and only the granulites of the Kan Complex have a median Sc/Th ratio of 1.0 ± 0.6 (Fig. 3f).

The ranges of the Co/Hf ratio are also broad enough: from <0.1 to 52–53 (Fig. 2g); i.e., they notably exceed two orders of magnitude. The values typical of the Average Archean Shale and PAAS (11.43 and 4.6, respectively) lie within the range (2–15) typical of most samples of Archean terrigenous rocks in our databank.

The median values of this ratio in approximately 80% of the reference Archean terranes are higher than the Co/Hf ratios of PAAS (Fig. 2g). At the same time, the metaterrigenous rocks of the Kan and Sharyzhalgai complexes and the Pongola Supergroup have these ratios lower than in PAAS.

The Ce/Cr ratio of the samples of our databank also significantly varies: the lowest value of this ratio is <0.05, and the highest one reaches 1.8 (Fig. 2g). Note that the vast majority of the samples of Archean metaterrigenous rocks show fairly low (<0.4) Ce/Cr ratios, and the Average Archean Shale of Taylor and McLennan has this ratio equal to 0.1. PAAS has a Ce/Cr ratio seven times higher: 0.73.

About 85% of the median values of the Ce/Cr ratio of various reference terranes from our databank are within the range of 0.5–0.35, and only the terrigenous rocks of the Kan and Sharyzhalgai complexes are characterized by values higher than that of PAAS (Fig. 3g).

The overwhelming majority of samples from our databank have a Th/Sc ratio no higher than 0.5–0.6 (this ratio of the Average Archean Shale is equal to 0.43 [11]) (Figs. 2a, 2h), and this ratio of PAAS is slightly higher (0.9). Although some Archean rocks exhibit ratios of 1.5–1.6, the total number of these samples is low.

More than 90% of the median values of the Th/Sc ratio calculated for various reference Archean terranes do not exceed 0.65 (Figs. 3a, 3h), and only the metaterrigenous rocks of the Kan Complex have median values of this ratio higher than in PAAS.

It is now pertinent to consider the problem as to how well is it possible to distinguish between Archean and post-Archean terrigenous rocks in Eu/Eu*–Gd_N/Yb_N, Sc/Th–La/Sm, Th/Sc–Sc, Ce/Cr–Co/Hf, Cr–Ni, Gd_N/Yb_N–Yb, La–Th, Cr–Th/Sc, Ce/Cr–Th/Sc, and other diagrams (Fig. 3).

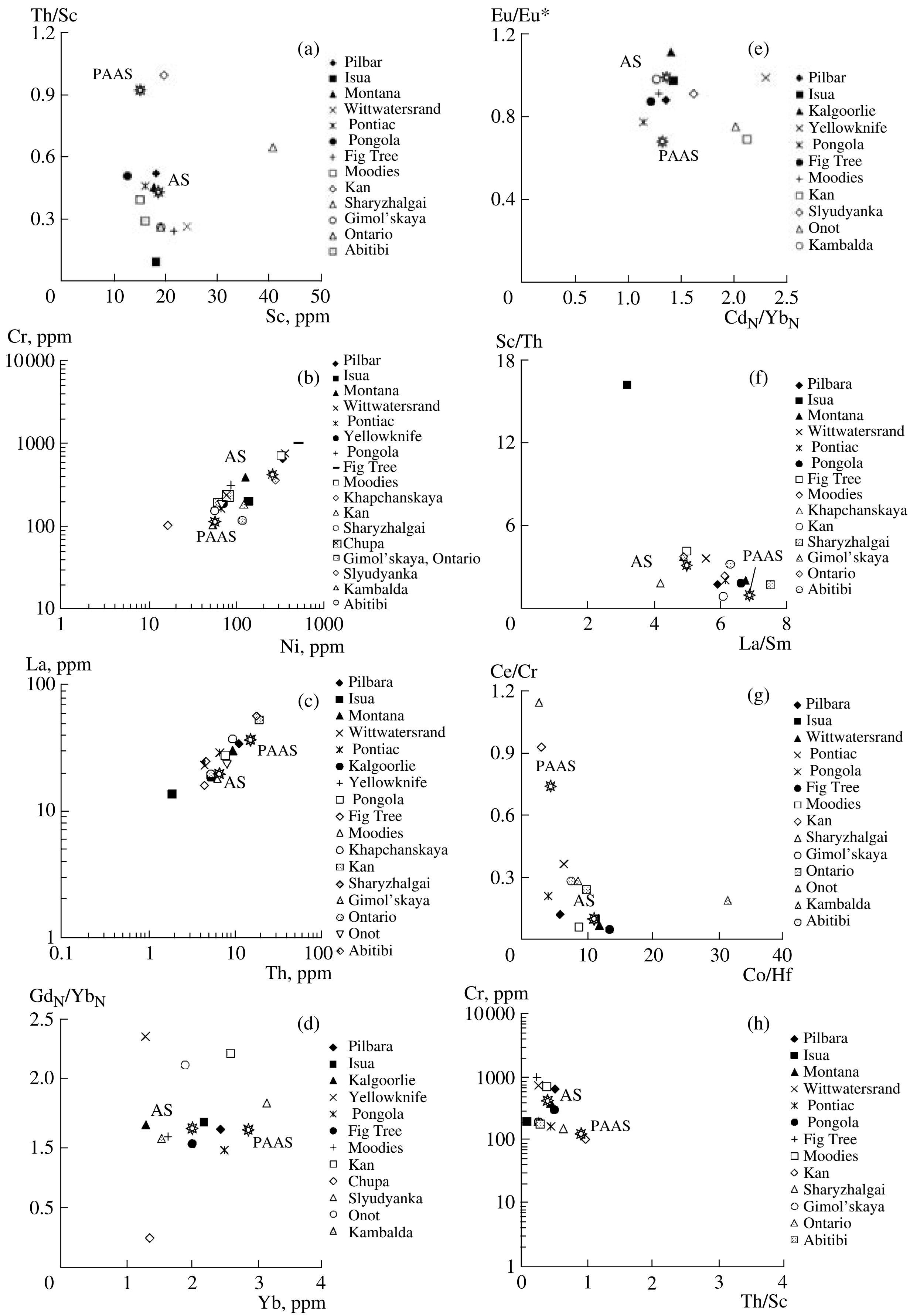
In the Eu/Eu*–Gd_N/Yb_N diagram, the median values of reference Archean terranes from our databank cluster within the region with 0.75–0.8 < Eu/Eu* < 1.1 and $1.15 < Gd_N/Yb_N < 2.35$. Note that the point of PAAS plots outside this region.

In the Sc/Th–La/Sm diagram, the data points of the median composition of Archean metaterrigenous rocks plot mostly within the region with 4 < La/Sm < 8 and Sc/Th < 5. The data points of both PAAS and the Average Archean Shale lie within this field.

In the Th/Sc–Sc diagram, most median compositions of Archean metaterrigenous rocks plot within the field corresponding to 12 < Sc < 25 ppm and Th/Sc from 0.1 to 1.0. The data point of PAAS lies at a much higher Th/Sc value, and only the granulites of the Kan Complex have this ratio higher than in PAAS (see above).

In the Ce/Cr–Co/Hf diagram, the vast majority of median values for the reference Archean terranes cluster within the compositional field with 4 < Co/Hf < 14 and 0.05 < Ce/Cr < 0.35. The PAAS point plots outside this field.

Fig. 3. Various geochemical diagrams for the median compositions of metaterrigenous rocks from various reference Archean terranes. See Fig. 2 for symbol explanations.



Th/Sc
(a)
PAAS
AS
Sc, ppm
Pilbar
Isua
Montana
Wittwatersrand
Pontiac
Pongola
Fig Tree
Moodies
Kan
Sharyzhalgai
Gimol'skaya
Ontario
Abitibi
Eu/Eu*
(e)
AS
PAAS
Cd_N/Yb_N
Pilbar
Isua
Kalgoorlie
Yellowknife
Pongola
Fig Tree
Moodies
Kan
Slyudyanka
Onot
Kambalda
Cr, ppm
(b)
AS
PAAS
Ni, ppm
Pilbar
Isua
Montana
Wittwatersrand
Pontiac
Yellowknife
Pongola
Fig Tree
Moodies
Khapchanskaya
Kan
Sharyzhalgai
Chupa
Gimol'skaya, Ontario
Slyudyanka
Kambalda
Abitibi
Sc/Th
(f)
AS
PAAS
La/Sm
Pilbara
Isua
Montana
Wittwatersrand
Pontiac
Pongola
Fig Tree
Moodies
Khapchanskaya
Kan
Sharyzhalgai
Gimol'skaya
Ontario
Abitibi
La, ppm
(c)
PAAS
AS
Th, ppm
Pilbara
Isua
Montana
Wittwatersrand
Pontiac
Kalgoorlie
Yellowknife
Pongola
Fig Tree
Moodies
Khapchanskaya
Kan
Sharyzhalgai
Gimol'skaya
Ontario
Onot
Abitibi
Ce/Cr
(g)
PAAS
AS
Co/Hf
Pilbara
Isua
Wittwatersrand
Pontiac
Pongola
Fig Tree
Moodies
Kan
Sharyzhalgai
Gimol'skaya
Ontario
Onot
Kambalda
Abitibi
Gd_N/Yb_N
(d)
AS
PAAS
Yb, ppm
Pilbara
Isua
Kalgoorlie
Yellowknife
Pongola
Fig Tree
Moodies
Kan
Chupa
Slyudyanka
Onot
Kambalda
Cr, ppm
(h)
AS
PAAS
Th/Sc
Pilbara
Isua
Montana
Wittwatersrand
Pontiac
Pongola
Fig Tree
Moodies
Kan
Sharyzhalgai
Gimol'skaya
Ontario
Abitibi

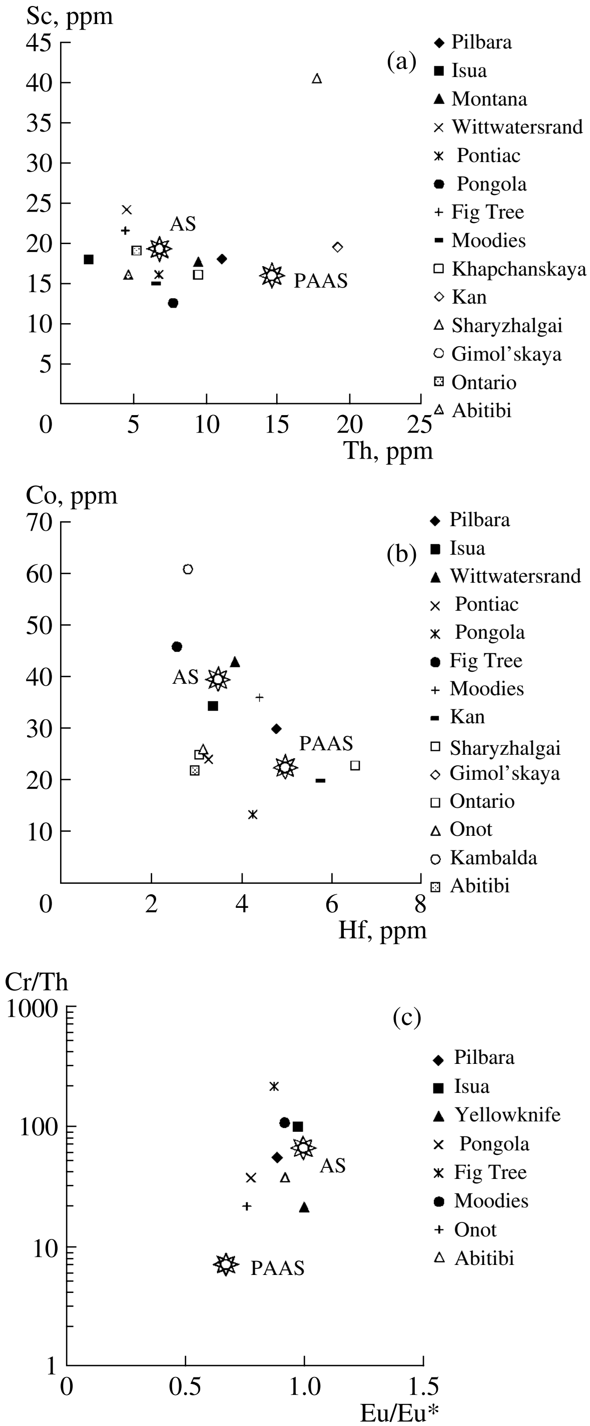


Fig. 4. (a) Sc–Th, (b) Co–Hf, and (c) Cr/Th–Eu/Eu* diagrams for the median compositions of metaterrigenous rocks from various reference Archean terranes. See Fig. 2 for symbol explanations.

In terms of median Cr and Ni concentrations, the field of most compositions of Archean fine-grained terrigenous rocks has the following limitations: 100 < Cr < 1000 and 40 < Ni < 550–600 ppm. The Cr and Ni concentrations definitely exhibit a positive correlation. The point of PAAS (110 ppm Cr and 55 ppm Ni) is located in the lowermost part of the field of Archean compositions.

The median compositional points of reference Archean metaterrigenous rocks do not define a compact field in the Gd_N/Yb_N–Yb diagram. The point of the Average Archean Shale is located in this diagram close to the center of the swarm of the data points of the reference terranes, whereas the point of PAAS, which has a higher Yb concentration, plots to the right of most Archean metaterrigenous rocks.

The La–Th diagram displays a clearly pronounced positive correlation between the median concentrations of these chemical elements in the reference Archean terranes. Their overwhelming majority is characterized by Th < 10–12 ppm and La < 40 ppm. PAAS has a Th concentration equal to 14.6 ppm and an La concentration of 38 ppm and, hence, was formed via the erosion of a somewhat more mature upper crustal material.

In the Cr–Th/Sc diagram, the median compositional points of the reference Archean metatesedimentary rocks define a compact field with 0.1 < Th/Sc < 0.7 and 150–160 < Cr < 1400 ppm. The data point of the Average Archean Shale lies close to the center of this field, while the point of PAAS has a lower Cr concentration and a higher Th/Sc ratio and lies outside this field.

In the Sc–Th diagram, the PAAS point plots outside the field of most of the median compositions of Archean metaterrigenous rocks (because of the high Th concentration in PAAS), which has the following parameters: 12 < Sc < 25 ppm and 2 < Th < 12 ppm. Only the granulites of the Kan and Sharyzhalgai complexes have Th concentrations higher than in PAAS (see above; Fig. 4a).

The differences between PAAS and the Average Archean Shale are pronounced less clearly in the Co–Hf diagram (Fig. 4b).

Conversely, because of the lower Cr/Th and Eu/Eu* ratios of PAAS than those of the Average Archean Shale and most reference Archean terrane, the point of PAAS lies in the Cr/Th–Eu/Eu* diagram away from the field of the median compositions of Archean metaterrigenous rocks (Fig. 4c).

The median Cr/Th ratios of metaterrigenous rocks from our databank vary from ×0.7 (Kan Complex) to ×52.5 PAAS (Isua). Very high values of more than ×10.0 PAAS of this parameter were shown by only five of the 26 reference Archean terranes (Isua, Wittwatersrand, Fig Tree, Moodies, and Belingwe), and the overwhelming majority of other median values of the Cr/Th ratios lie outside the range of 1.1–7.4–8.5 PAAS (Fig. 5). It is interesting to note that the median Cr/Th ratio of the metaterrigenous rocks of the Western Gneiss Terrane in Australia is exactly equal to this ratio in PAAS.

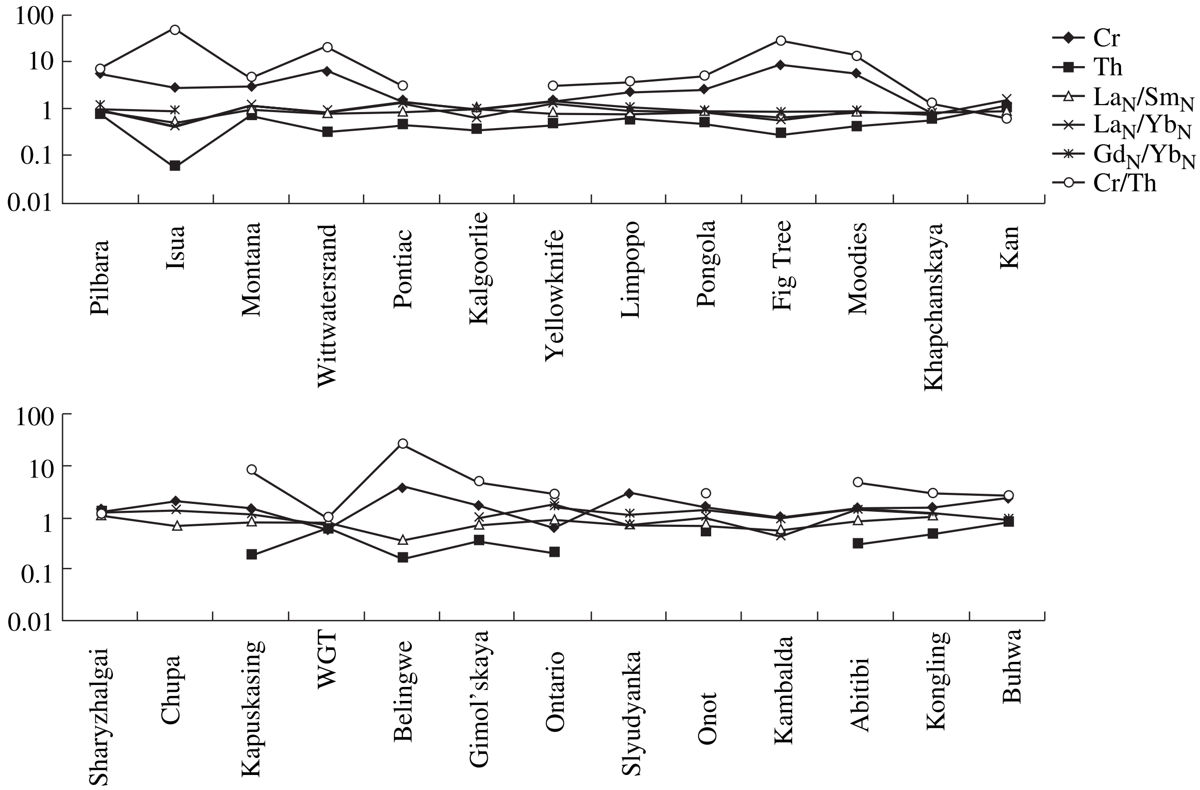


Fig. 5. Variations in the PAAS-normalzied median concentrations (ppm) of Cr and Th and the Cr/Th, La_N/Yb_N, La_N/Sm_N, and Gd_N/Yb_N ratios of metaterrigenous rocks from various reference Archean terranes.

The normalization of such REE parameters as La_N/Yb_N, La_N/Sm_N, and Gd_N/Yb_N to PAAS reveals another interesting feature of the metaterrigenous rocks of reference Archean terranes: with only a few exceptions, all of them have these ratios very close to those in PAAS (Fig. 5). For example, the La_N/Yb_N ratio varies mostly within the range of 0.74–0.84–1.30–1.38 PAAS. The rocks of the Isua and Kambalda blocks have much lower median values (0.45–0.47) of this ratio, and some terranes (Ontario, Abitibi, and Kan complexes) have this parameter more than 1.5 times higher than in PAAS. The vast majority of the reference Archean terranes have median Gd_N/Yb_N ratios ranging from 0.88 to 1.18 PAAS, and only the metaterrigenous rocks of the Yellowknife Supergroup, Kan and Onot complexes, Kongling Group, and rocks from Ontario have slightly higher values of this ratio. The differences between the median La_N/Sm_N values of PAAS and most of the reference Archean terranes are even smaller. Most of them (~70%) lie within the range of 0.7–0.11 PAAS, although some of them have La_N/Sm_N values as low as ×0.37 (Belingwe) and ×0.35 (Isua) PAAS.

Figures 6 and 7 display the median concentrations of some trace elements and their ratios for various reference Archean territories normalized to the corresponding values for the Average Archean Shale and PAAS. The analysis of these figures led us to draw at least two conclusions.

First, the median concentrations of Sc, V, Cr, Co, Ni, Nb, La, Ce, Th, and U in Archean metaterrigenous rocks significantly vary relative to the corresponding values for the Average Archean Shale (from ×0.2 to ×10); whereas the median concentrations of Eu, Yb, and Hf vary not as significantly (from 0.7 to 2). The median values of the La_N/Yb_N, Gd_N/Yb_N, Eu/Eu*, La/Sm, Co/Hf, Ce/Cr, and Th/Sc also show a significant scatter.

Second, the rocks of Archean reference complexes contain three groups of elements with different ratios to their concentrations in PAAS. The first group comprises elements whose median concentrations are commonly higher than in PAAS; these are Sc, Cr, Co, and Ni. The second group includes Nb, La, Ce, Yb, Hf, Th, and U, whose median concentrations in the reference Archean terranes are practically always lower than in PAAS. Finally, the third group consists of V, Sm, and Eu, whose concentrations can be either higher or lower than in PAAS. The negative Eu anomalies in Archean metaterrigenous rocks range from ×1.06 to ×1.7 PAAS. The median values of the La/Sm, Ce/Cr, and Th/Sc ratios of the reference Archean terranes are almost always lower than in PAAS, whereas the Co/Hf ratio is higher.

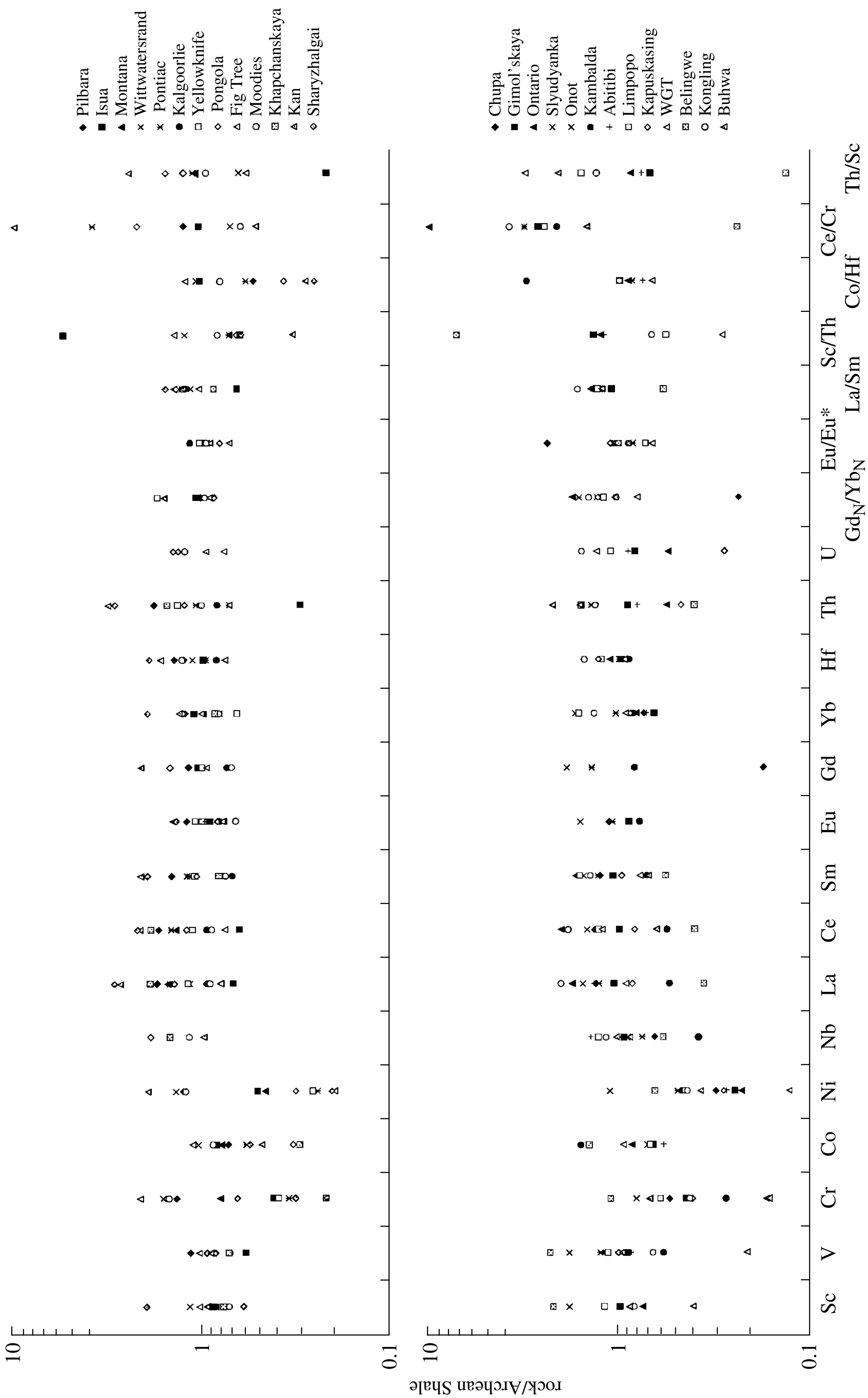


Fig. 6. Variations in the median concentrations of some trace elements normalized to the Average Archean Shale and in some ratios of these elements in metaterrigenous rocks from various reference Archean terranes.

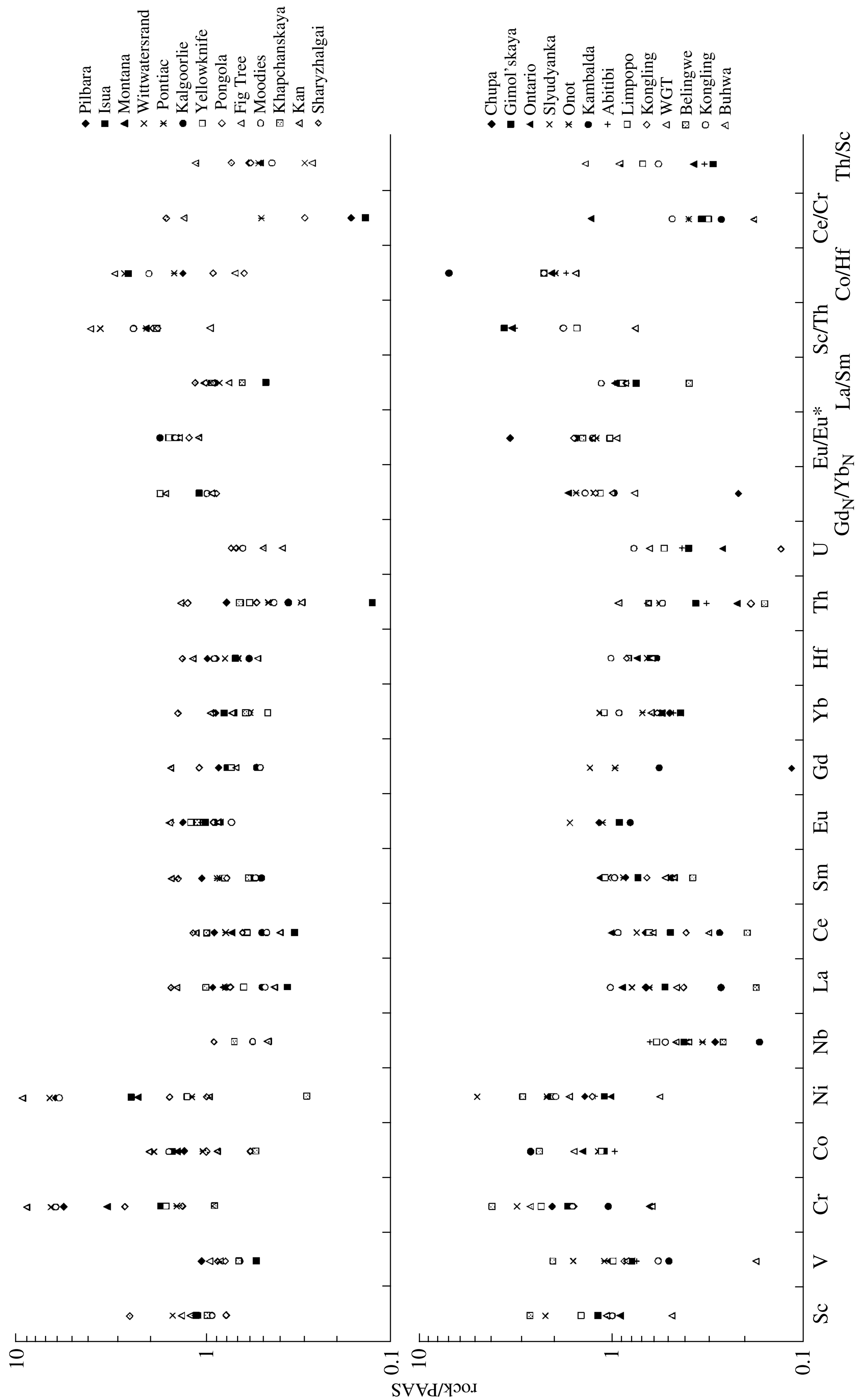


Fig. 7. Variations in the median concentrations of some trace elements normalized to PAAS and in some ratios of these elements in metaterrigenous rocks from various reference Archean terranes.

CONCLUSIONS

Summarizing the data and considerations presented above, the following conclusions concerning the geochemical constraints of Archean metaterrigenous rocks can be drawn.

The main conclusion following from the results of our research is that the available databank did not allow us to identify any one parameter (or a few parameters) suitable to reliably (i.e., with a confidence of 90–95%) distinguish between Archean and post-Archean fine-grained terrigenous rocks. In the overwhelming majority of the analyzed situations (including such seemingly "reliable" ones as distinguishing between Late and Early Archean compositions in Cr–Ni and La–Th diagrams [11]), the points of the Average Archean Shale and PAAS plotted within the fields of points of the individual analyses of Archean metaterrigenous rocks.

If the confidence level is diminished to approximately 80–85%, it can be seen than the bulk of the individual data points of Archean metaterrigenous rocks have the following geochemical parameters: (1) Th/Sc < 0.6–0.7, (2) Ce/Cr < 0.6, and (3) Eu/Eu* > 0.70–0.75. The latter testifies that Archean metamorphosed terrigenous complexes include both rocks practically devoid of Eu anomalies and those with clearly pronounced Eu anomalies, although the values of these anomalies are not as significant as in post-Archean sedimentary sequences.

If the median concentrations of some trace elements and their ratios are considered, the constraints specified above should be modified as follows: (1) Th/Sc < 0.55, (2) Ce/Cr < 0.4, (3) Cr/Th > 25 (or $(Cr/Th)_{AR\,rock}$/PAAS > 3.0, which is practically the same), and (4) Th < 12 ppm.[9]

When compared with PAAS (as the standard reference composition of post-Archean aluminosilicate clastic rocks), Archean metaterrigenous rocks display higher median concentrations of Cr and Ni and the Eu/Eu*, Sc/Th, Cr/Th, and Co/Hf ratios, whereas the Nb, La, Ce, Yb, Hf, Th, and U concentrations and the La/Sm and Ce/Cr are lower in PAAS.

The REE patterns of Archean metaterrigenous rocks show some distinctive features but generally seem to be not principally different from that of PAAS.

For example, the median La_N/Yb_N ratios of reference Archean terranes can be either higher or lower than in PAAS, which is definitely predetermined by the proportions of silicic and basic + ultrabasic rocks in the eroded source material. The median Gd_N/Yb_N ratios of about 60% of the Archean reference terranes in our databank are somewhat higher than in PAAS, but approximately 30% of these terranes show a Gd_N/Yb_N ratio lower than in PAAS. Only the metaterrigenous rocks of the Kan block and Ontario Province show median Gd_N/Yb_N ratios higher than 2.0, which suggests significant HREE depletion and is not a distinctive feature of Archean metaterrigenous rocks but, similarly to the La_N/Yb_N ratio, depends on the local geological situation. Finally, the median La_N/Sm_N ratio of the vast majority of Archean metaterrigenous rocks is slightly lower than in PAAS and likely implies that the Archean protoliths were somewhat immature.

It follows that only a complex analysis of the geochemistry of terrigenous rocks, with regard for all the considerations presented above, can provide a clue to understanding the genesis of Archean sedimentary sequences.

[9] Recall that the median Cr/Th ratio for the rocks of the Western Gneiss Terrane of Australia is equal to that of PAAS (see above).

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