



# Article Source Characteristics of the Carboniferous Ortokarnash Manganese Deposit in the Western Kunlun Mountains

Bang-Lu Zhang <sup>1,2,3</sup>, Zhi-Cheng Lv <sup>1,2,3</sup>, Zhi-Guo Dong <sup>4,5,6</sup>, Xin Zhang <sup>4,5,6</sup>, Xiao-Fei Yu <sup>1,2,3</sup>, Yong-Sheng Li <sup>1,2,3</sup>, Shi-Min Zhen <sup>1,2,3</sup> and Chang-Le Wang <sup>4,5,6,\*</sup>

- <sup>1</sup> Development and Research Center, China Geological Survey, Beijing 100037, China; zhangbanglu2008@126.com (B.-L.Z.); zhichenglv@163.com (Z.-C.L.); xfyu@jlu.edu.cn (X.-F.Y.); liysh1983@126.com (Y.-S.L.); zhenshimin0001@163.com (S.-M.Z.)
- <sup>2</sup> School of Earth Sciences and Resources, China University of Geosciences, Beijing 100083, China
- <sup>3</sup> Mineral Exploration Technical Guidance Center, Ministry of Natural Resources of the People's Republic of China, Beijing 100037, China
- <sup>4</sup> Key Laboratory of Mineral Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China; dongzhiguo@mail.iggcas.ac.cn (Z.-G.D.); zhangxin\_cq@163.com (X.Z.)
- <sup>5</sup> Institutions of Earth Science, Chinese Academy of Sciences, Beijing 100029, China
- <sup>6</sup> University of Chinese Academy of Sciences, Beijing 100049, China
- Correspondence: wangcl@mail.iggcas.ac.cn

Abstract: The specific source of ancient sedimentary manganese (Mn) deposits is commonly complex. Here we use systematic major and trace element data with strontium (Sr) and neodymium (Nd) isotopic analyses of the Ortokarnash Mn(II) carbonate ores and associated carbonate rocks from the Upper Carboniferous Kalaatehe Formation (ca. 320 Ma) in order to constrain the Mn source. This formation consists of three members: the first member is a volcanic breccia limestone, the second member is a sandy limestone, and the third member is a black marlstone with the Mn(II) carbonate interlayers. Petrographic observations in combination with low Al<sub>2</sub>O<sub>3</sub> (<3.0 wt%) and Hf (<0.40 ppm) contents and the lack of correlations between the Al<sub>2</sub>O<sub>3</sub> and  ${}^{87}$ Sr / ${}^{86}$ Sr ratios as well as  $\epsilon$ Nd(t) values demonstrate a negligible influence of terrigenous detrital contamination on both Sr and Nd isotopic compositions of the Mn(II) carbonate ores. The Sr isotopes of Mn(II) carbonate ores are most likely affected by post-depositional alteration, while Nd isotopes remain unaltered. The initial <sup>87</sup>Sr/<sup>86</sup>Sr ratios in the associated carbonate rocks are likely the result of a mixture of the chemical components (i.e., seawater) and the Al-rich components (e.g., volcanoclastic material), while the detrital effects on Nd isotopes are negligible. In addition, both Sr and Nd isotopes in these non-mineralized wall rocks remained unchanged during post-depositional processes. The relatively low Th/Sc ratios and positive  $\varepsilon$ Nd(t) values suggest that the aluminosilicate fraction in the calcarenite and sandy limestone was mainly derived from the weathering of a depleted mafic source, representing the riverine input into the seawater. Given that the Mn(II) carbonate ores are characterized by negative  $\epsilon$ Nd(t) values, these suggest that seafloor-vented hydrothermal fluids derived from interaction with the underlying old continental crust mainly contribute to the source of the Mn(II) carbonates.

**Keywords:** source; strontium and neodymium isotopes; Mn(II) carbonate mineralization; Ortokarnash Mn ore deposit; West Kunlun Mountains

## 1. Introduction

Sedimentary manganese (Mn) ore deposits account for more than 90% of the total endowment of land-based economic Mn resources [1]. The precise source of Mn in ancient deposits is commonly complex. Generally, hydrothermal and terrestrial weathering processes serve as primary sources of Mn in the depositional basins [2,3]. In the modern oceans, dissolved Mn(II) concentration maxima occur in the oxygen minimum zone at the depth ranging from 2000 to 3000 m, due to atmospheric dust [4–6], shelf sediments [7–10], and



Citation: Zhang, B.-L.; Lv, Z.-C.; Dong, Z.-G.; Zhang, X.; Yu, X.-F.; Li, Y.-S.; Zhen, S.-M.; Wang, C.-L. Source Characteristics of the Carboniferous Ortokarnash Manganese Deposit in the Western Kunlun Mountains. *Minerals* 2022, *12*, 786. https:// doi.org/10.3390/min12070786

Academic Editor: Francesco Dela Pierre

Received: 6 May 2022 Accepted: 15 June 2022 Published: 21 June 2022

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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). hydrothermal vents [11–14]. Mass balance considerations suggested that the present-day input of Mn into the oceans is in balance with its deposition in Mn nodules and sediments, with perhaps 90% of the input being from hydrothermal sources [15]. Whereas, based on a statistical analysis of global sedimentary Mn ore deposits, Maynard [1] claimed that in contrast to modern deep-sea nodules, which likely have a large component of sediment-derived Mn, almost all economic Mn ores are ultimately or directly derived from hydrothermal vents. For example, considering a mid-ocean ridge or a failed rift basin setting, Gutzmer [16] argued for a hydrothermal origin of the giant Paleoproterozoic Kalahari manganese field of the Hotazel Formation (~2.4 Ga [17]). Geochemical and Sr-Nd isotopic characteristics of the Cryogenian (664–653 Ma) Datangpo Mn(II) carbonate ores in South China indicate that the compositions are at least partly derived from hydrothermal sources [18]. Similar conclusions have been proposed for other Neoproterozoic Mn ore deposits from Namibia (the Chuos Formation at Otjosondu [19–21]) and Brazil (the Santa Cruz Formation at Urucum [22]).

On the other hand, the supply of Mn from terrestrial sources cannot be ignored. Manganese is present exclusively in divalent forms in a wide range of igneous minerals in which it substitutes for iron [23]. It averages at 980 ppm or about 0.1% in a variety of igneous rocks [24]. Thus, silicate weathering provides a substantial source of Mn(II) to surface and ground waters [23,25,26]. Although it is difficult for dissolved Mn(II) to transport in an ionic solution in an oxygenated environment for a long distance, manganese can be transported as oxyhydroxide particulates or colloids [27–30], and its gross riverine discharge to the oceans is considerable [2,31,32]. Accordingly, terrestrial weathering provides materials for the formation of some ancient Mn deposits. For example, based on the lowest units of the Santa Cruz Formation associated with clastic sediments with dropstones, the metals of the Urucum deposit are presumed to have been derived from continental weathering [33,34]. In order to explain the restricted spatial and temporal nature of the giant Molango deposit of the Kimmeridgian age, Okita [35] favored the fluvial transport of Mn derived from a continental source to the depositional basin. The metals of the giant sedimentary Mn ore deposits of the Early Oligocene age bordering the Black Sea in Georgia (Chiatura [36]), Ukraine (Nikopol [37]), and Bulgaria (Obrochishte [38]) have been proposed to be derived from terrestrial weathering [3,27,37–39]. In brief, volcanic/hydrothermal activity is commonly considered to be the main source of Mn in the depositional basin, while a contribution from terrestrial weathering is also proposed despite the lack of robust geochemical evidence.

The Malkansu Mn carbonate metallogenic zone in the West Kunlun orogenic belt is hosted in the Carboniferous sedimentary rocks of the Kalaatehe Formation (Figure 1A). Among them, Mn ore deposits are under-prospected, and the Ortokarnash is the only orebody being actively mined, with the highest-grade Mn carbonate ores (avg. Mn > 37% by weight) identified in China [40]. Previous studies have provided significant information about the geological and geochemical characteristics of the Mn-bearing sequences of the Kalaatehe Formation [40–43]. Based on detailed lithological observations combined with rare earth elements and C isotope studies, Zhang et al. [44] suggested that both the Mn ores and the associated carbonate rocks at Ortokarnash were possibly deposited under an oxic water column, and the Mn(II) carbonates were the result of dissimilatory Mn(III/IV) oxide reduction during sedimentary diagenesis. However, the source of Mn ore intervals in the Kalaatehe Formation is still unclear.

In this study, based on a detailed petrographic study, Sr and Nd isotope data were generated for Mn(II) carbonate ores and associated carbonate rocks of the Ortokarnash deposit. These data, combined with elemental data published previously, served to more fully characterize the geochemical composition of the ore deposit in order to better understand both the geochemical background of the depositional basin and the source of Mn, as well as the mechanism of the Mn mineralization.





# 2. Geological Setting

The West Kunlun Orogenic Belt (WKOB)—the westward extension of the central orogenic belt in China [45,46] is bounded by the Tarim Basin to the north, the Tibetan Plateau to the south, and the Pamir Plateau to the west [47,48], and has been offset from the East Kunlun Orogen and the Songpan-Ganzi terrane by the Cenozoic Altyn sinistral strike-slip fault to the east (Figure 1A) [49–51]. As one of the major tectonic units forming the northern boundary of the western Tibetan Plateau, WKOB underwent long-term crustal assemblage and accretion between early Paleozoic and Mesozoic in response to the evolution of the Proto- to Palaeo-Tethys Ocean [47,52–55], and was overprinted by Cenozoic volcanism accompanying India–Asia convergence [52,56–58].

The WKOB is divided into three main units based on their tectonic characteristics and stratigraphic associations, from north to south, consisting of the (a) North Kunlun Terrane (NKT), (b) South Kunlun Terrane (SKT), and (c) Tianshuihai Terrane (TSHT) (Figure 1A) [47,59–61]. NKT and SKT are separated by the early Paleozoic ophiolite-bearing Kudi-Qimanyute suture (Figure 1A), which is believed to extend northwest toward the town of Oytagh [62]. The Karakax fault (Kangxiwa fault as described by Zhang et al. [63] is regarded as the suture zone between SKT and TSHT, which trends E–W in the eastern section of the WKOB and switches off by the Cenozoic N–S-trending Tashikoergan fault to the west [64–66].

The Malkansu Mn metallogenic zone is tectonically situated in the NKT, at the junction of the western margin of the Tarim basin and the WKOB (Figure 1B) [40,63]. Although the timing for the formation of the Late Devonian to Early Permian sedimentary sequence in the NKT remains controversial [47,52,67–69], a recent study suggested that these shallow marine carbonate and clastic rocks represent a late Paleozoic to early Mesozoic back-arc basin sequence and were deposited in response to the northward subduction of the Paleo-Tethys Ocean [63]. Moreover, geochemical studies of the Carboniferous volcanic rocks have indicated that the NKT was a back-arc extensional environment during the early Carboniferous [70,71].

The Mn metallogenic zone is roughly 60 km (west to east) in length by 2 km (north to south) in width and encompasses one active (Ortokarnash) and two prospecting (Muhu and Malkantu) mines as well as several manganese mineralization spots (Figure 1B). The exposed strata include: (a) a Cambrian to Silurian metamorphic sequence in the SKT, (b) a Carboniferous to Permian volcano-sedimentary sequence in the NKT, and (c) a Cretaceous

to Paleogene–Neogene marine and non-marine sequence in the Tarim block. The Cambrian metamorphic rocks of the Bulunkuole Group and the Silurian metamorphic rocks of an unnamed group are widely distributed in the southern part of the district and occur as a fault contact with the Carboniferous–Permian sequence to the north along the regional Kobailey–Muzaling fault (Fk) (Figure 1B). The late Mesozoic to Cenozoic terrigenous sedimentary rocks cover the northern portion of the district, which tectonically belongs to the Tarim block. Both the Cretaceous strata and the Paleogene–Neogene sequence are in contact with the Carboniferous–Permian sequence to the south along the regional Uchiburi fault (Fu) (Figure 1B).

The early Carboniferous basalt flows and associated pyroclastic rocks of the Wuluate Formation largely cover the eastern portion of the district. Zircons from these basalts yield  $^{206}$ Pb/ $^{238}$ U ages of 326.6  $\pm$  1.3, 327.3  $\pm$  2.6, and 331.5  $\pm$  1.5 Ma ([40]; Figure 2), respectively, indicating that the volcanism occurred in the Malkansu area at the end of the Mississippian. The Upper Carboniferous Kalaatehe Formation unconformably overlies the Wuluate Formation and has been subdivided, from bottom to top, into three members: (1) the first member consists of limestone with volcanic-bearing breccia, (2) the second member comprises sandy limestone, and (3) the third member consists of marlstone with either one or two Mn interlayers (Figure 2; [41]).



**Figure 2.** Stratigraphic succession for the Carboniferous to Permian volcano-sedimentary sequence of the Malkansu back-arc basin, highlighting the Kalaatehe Formation composed of three members and the interval of manganese mineralization (modified after [44]). Previously published age constraints are also listed, and these data are from [40,72,73].

The gray-white volcanic breccia-bearing limestone is interlayered with yellowishgreen calcarenite in the uppermost 20 m. The calcarenites are primarily composed of micritic carbonates (60%) and volcanic debris (25%), with minor pyroxene, feldspar, and quartz crystals (<10%), cemented by micrite and mud matrix (Figure 3A). The second member comprises interlayered argillaceous limestone and thickly bedded sandy limestone. The sandy limestone is composed mainly of sand-sized micritic carbonates grains (>60%), quartz crystals, and chalcedony or opal (40%), with minor volcanic and silicate mineral debris (feldspar with small amounts of chlorite and biotite; Figure 3B). The interbedded layers of grey-black argillaceous limestone with homogenous structure are primarily composed of micrite and mud matrix with minor subangular opal/chalcedony grains (Figure 3C). The third member consists primarily of marlstone with minor layers of argillaceous limestone, and contains either one or two manganese carbonate layers. The marlstone is dark gray to black, organic-rich, and is composed of fine-grained micritic carbonates, silicate mineral debris (i.e., feldspar, chlorite, and minor biotite), and quartz crystals or chalcedony (Figure 3D). Pyrite framboids and solid bitumen grains also commonly occurred within the organic-rich marlstone. The Mn(II) carbonate ores are massive in structure, while polished fresh ores are tan and darker brown or black in color, and laminated (Figure 3E). Rhodochrosite  $(Mn(Ca,Mg)CO_3/Mn(Fe)CO_3)$  is the most abundant mineral and is almost the only carbonate phase that occurs in this ore zone (Figure 3F). Small amounts of Mn(II)-rich silicate (e.g., friedelite), Mn(II)-rich aluminosilicate (e.g., Mn(II)-rich chlorite), manganoan calcite, alabandite, and Mn-Fe oxides are observed.

Zircons from the volcanic breccia of the first member yield a  $^{206}$ Pb/ $^{238}$ U age of 322.9  $\pm$  1.8 Ma [73], providing a robust and maximum depositional age of the Kalaatehe Formation. Samples of the approximately 6-m-thick ore layers yield a Re-Os age of 320.3  $\pm$  6.6 Ma, representing the mineralization age of the Ortokarnash Mn ore deposit [73]. In this sedimentary sequence, samples from the hanging-wall marlstones yield a Re-Os age of 316.3  $\pm$  8.0 Ma, representing the minimum mineralization age for this deposit (Figure 2 [73]). The Permian Maerkanque–Kusaishan Formation, consisting of a gray-purple conglomerate, andesitic tuff, and minor andesite at the base, unconformably overlies the Carboniferous Kalaatehe Formation (Figure 2). In the absence of geochronological dates, the overlying Maerkanque–Kusaishan Formation is considered to have been deposited in the lower Permian based on the observed fusulinids *Dunbarinella* sp. and brachiopod *Stenoscisma* sp. fossil occurrences [72].



**Figure 3.** Photomicrographs showing representative textures and petrographic features of the Upper Carboniferous Kalaatehe Formation at the Ortokarnash mine. (**A**). Interlayered fine calcarenite from the topmost 20 m of the volcanic breccia limestone of the first member (crossed polarizers). (**B**). Homogeneous sandy limestone of the second member (crossed polarizers). (**C**). Interlayered slightly laminated argillaceous limestone of the second member (crossed polarizers). (**D**). Homogeneous marlstone of the third member (crossed polarizers). (**E**). Crenulated to wavy laminations in manganese carbonate ore; note minor manganoan calcite veins (crossed polarizers). (**F**). Two generations of rhodochrosite occurring in the manganese ore, with the former containing minor calcium and magnesium, while the latter incorporates iron (backscattered electron image).

## 3. Sampling and Analytical Methods

Samples were obtained from both the open pit of the Ortokarnash deposit and underground tunnels of the Ortokarnash mine. Sampling efforts were concentrated on the main mining location, where the ore was of high grade and the ore layer was the thickest (with a maximum thickness of about 7 m). In addition, this location allowed for the most complete access to a continuous stratigraphic section of associated rocks underlying and overlying the Mn ore.

A detailed petrographic examination using transmitted and reflected light was carried out to determine the mineralogy and paragenesis of all manganese ore and its associated rock samples. Scanning electron microscopy equipped with energy dispersive spectrometry (SEM-EDS) was used to document the small-scale relationships between the textures and measure the elemental abundances. Electron microprobe analyses (EMPA) for the Mn ore samples were performed using a JEOLJXA-8100 electron microprobe operating at 15 kV with a 20-nA current and a focused ~1-µm electron beam. Both experiments were conducted at the Institute of Geology and Geophysics, Chinese Academy of Sciences in Beijing.

Representative samples, including six Mn ore and 18 wall-rock samples, were selected for geochemical analysis. Samples were broken into chips, with any chips showing evidence of secondary veins or surface weathering removed, and the remaining sample was then ground into a fine powder in a tungsten steel grinding mill. All prepared powder samples were stored in the drying dish for further analysis.

Geochemical analysis for major and trace elements was already performed by Zhang et al. [44]; thus, this study focused on the isotope geochemistry. The strontium (Sr) and neodymium (Nd) isotopic determination of whole-rock samples followed procedures similar to those described by Li et al. [74,75]. Whole-rock powders for Sr and Nd isotopic analyses were dissolved in a Savillex Teflon screw-top capsule using  $HF + HNO_3 + HClO_4$ dissolution. Strontium and Nd were separated using the classical two-step ion-exchange chromatographic method and measured using a Thermofisher Triton Plus multi-collector thermal ionization mass spectrometer at the Institute of Geology and Geophysics, Chinese Academy of Sciences in Beijing. The whole procedure blank was lower than 250 pg for Sr and 100 pg for Nd. The isotopic ratios were corrected for mass fractionation by normalizing to  ${}^{88}$ Sr/ ${}^{86}$ Sr = 8.375209 and  ${}^{146}$ Nd/ ${}^{144}$ Nd = 0.7219, respectively. The international standard samples, NBS-987 and JNdi-1, were employed to evaluate instrument stability during the period of data collection. The measured values for the NBS-987 Sr standard and JNdi-1 Nd standard were  ${}^{87}$ Sr /  ${}^{86}$ Sr = 0.710259  $\pm$  0.000009 (n = 2, 2SD) and  ${}^{143}$ Nd/ ${}^{144}$ Nd =  $0.512102 \pm 0.000002$  (n = 2, 2SD), respectively. USGS reference material BCR-2 was measured to monitor the accuracy of the analytical procedures, with the following results:  $^{87}$ Sr/ $^{86}$ Sr = 0.705024  $\pm$  0.000013 and  $^{143}$ Nd/ $^{144}$ Nd = 0.512620  $\pm$  0.000011. The  $^{87}$ Sr/ $^{86}$ Sr and <sup>143</sup>Nd/<sup>144</sup>Nd data of BCR-2 show good agreement with previously published data by the TIMS technique [74,75]. The <sup>87</sup>Rb/<sup>86</sup>Sr and <sup>147</sup>Sm/<sup>144</sup>Nd ratios were calculated using the Rb, Sr, Sm, and Nd contents reported by Zhang et al. [44].

## 4. Results

# 4.1. Major and Trace Elements

The major, trace, and REE elemental compositions of the whole-rock samples of the study were reported by Zhang et al. [44] and are compiled in Table 1. Briefly, six analyzed Mn(II) carbonate ores are characterized by high MnO (54.43  $\pm$  1.52 wt%) and low Fe<sub>2</sub>O<sub>3</sub> (total Fe; 1.27  $\pm$  0.36 wt%) contents. Other oxide contents, such as SiO<sub>2</sub> (7.33  $\pm$  2.42 wt%), Al<sub>2</sub>O<sub>3</sub> (1.63  $\pm$  0.76 wt%), CaO (1.74  $\pm$  0.81 wt%), MgO (2.80  $\pm$  1.00 wt%), and P<sub>2</sub>O<sub>5</sub> (0.55  $\pm$  0.11 wt%), are relatively low, and the Na<sub>2</sub>O, K<sub>2</sub>O, and TiO<sub>2</sub> are generally lower than 0.2 wt%. The non-mineralized carbonate rocks, however, have remarkably low MnO (0.60  $\pm$  0.67 wt%) and relatively high Fe<sub>2</sub>O<sub>3</sub> (total Fe; 5.36  $\pm$  1.39 wt%) contents compared to those of the Mn(II) carbonate ores (Table 1). Other oxide contents (e.g., SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and CaO) are mainly controlled by lithology. For example, the SiO<sub>2</sub> is higher (46.92–54.72 wt%, avg. 51.17 wt%) in the marlstone, while the CaO is lower (9.66–13.85 wt%, avg. 11.25 wt%)

than in the sandy limestone and calcarenite, in which the abundances of SiO<sub>2</sub> and CaO are 27.94–42.73 wt% (avg. 35.90 wt%) and 16.05–26.40 wt% (avg. 19.94 wt%), respectively. Both marlstone and sandy limestone have nearly equal contents of Al<sub>2</sub>O<sub>3</sub>, with mean values of 11.22 wt% and 10.25 wt%, respectively. Interlayered argillaceous limestone, however, has the highest contents of CaO (25.90–38.60 wt%, avg. 33.88 wt%) among the non-mineralized samples.

Table 1. Compiled major (wt%) and trace element	(ppm) concentrations for samples of the Upper
Carboniferous Kalaatehe Formation.	

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$ \begin{array}{c} \dot{Cr} & 60.87 & 41.87 & 50.61 & 58.05 & 35.14 & 53.51 & 24.48 & 107.91 & 143.25 & 88.47 & 114.70 & 138.92 \\ \dot{Co} & 85.7 & 55.8 & 68.5 & 7.17 & 40.1 & 95.5 & 52.2 & 18.63 & 24.09 & 16.40 & 19.65 & 14.69 \\ \dot{Ni} & 26.30 & 9.77 & 19.68 & 15.60 & 9.02 & 24.61 & 12.15 & 48.82 & 39.53 & 47.49 & 61.00 & 47.34 \\ \dot{Cu} & 5.32 & 0.58 & 0.44 & 0.91 & 0.59 & 0.66 & 12.36 & 70.39 & 44.24 & 56.98 & 71.46 & 18.68 \\ \dot{Rb} & 1.20 & 0.69 & 0.73 & 0.69 & 0.43 & 0.66 & 3.46 & 5.72 & 0.93 & 29.74 & 22.47 & 23.10 \\ \dot{Sr} & 85.14 & 86.27 & 44.48 & 30.90 & 20.32 & 19.74 & 974.53 & 710.27 & 474.38 & 638.87 & 638.66 & 420.14 \\ \dot{Ba} & 14.78 & 11.15 & 64.9 & 51.2 & 0.47 & 3.43 & 46.92 & 115.24 & 22.20 & 654.05 & 456.22 & 502.44 \\ \dot{Zr} & 17.22 & 8.75 & 15.03 & 14.98 & 11.18 & 18.63 & 15.16 & 39.16 & 33.75 & 43.80 & 50.38 & 26.37 \\ \dot{Hf} & 0.32 & 0.11 & 0.31 & 0.27 & 0.10 & 0.40 & 0.40 & 1.10 & 1.01 & 1.34 & 1.51 & 0.09 \\ Pb & 7.34 & 1.04 & 2.22 & 3.56 & 2.66 & 5.17 & 2.94 & 11.82 & 4.23 & 8.85 & 12.03 & 4.37 \\ Pb & 7.34 & 1.04 & 2.22 & 3.56 & 2.66 & 5.17 & 2.94 & 11.82 & 4.23 & 8.85 & 12.03 & 4.37 \\ Pr & 4.04 & 0.22 & 0.04 & 2.33 & 1.93 & 2.86 & 2.11 & 2.06 & 1.95 & 2.32 & 2.83 & 0.94 \\ La & 16.50 & 9.96 & 19.70 & 19.23 & 11.22 & 17.11 & 13.34 & 7.66 & 6.75 & 8.03 & 9.72 & 2.44 \\ Ce & 112.53 & 70.32 & 121.36 & 128.87 & 64.30 & 105.46 & 23.55 & 18.82 & 14.18 & 17.01 & 19.93 & 4.76 \\ Pr & 4.04 & 2.32 & 4.23 & 4.25 & 2.43 & 3.74 & 2.68 & 2.10 & 1.70 & 2.02 & 2.38 & 0.70 \\ Nd & 18.79 & 10.02 & 17.48 & 18.10 & 9.95 & 15.94 & 11.16 & 9.04 & 7.45 & 8.67 & 10.13 & 3.17 \\ Pr & 4.04 & 2.32 & 4.22 & 4.25 & 2.43 & 3.74 & 2.68 & 2.10 & 1.70 & 2.02 & 2.38 & 0.70 \\ Nd & 18.79 & 10.02 & 17.48 & 18.10 & 9.95 & 15.94 & 11.16 & 9.04 & 7.45 & 8.67 & 10.13 & 3.17 \\ Pr & 4.04 & 2.32 & 4.22 & 4.25 & 2.43 & 3.74 & 2.68 & 2.10 & 1.70 & 1.02 & 2.28 & 0.70 \\ Nd & 18.79 & 10.02 & 17.48 & 18.10 & 9.95 & 15.94 & 11.16 & 9.04 & 7.45 & 8.67 & 10.13 & 3.17 \\ Pr & 4.04 & 2.32 & 4.26 & 0.74 & 0.43 & 0.58 & 0.33 & 0.43 & 0.34 & 0.40 & 0.44 & 0.21 \\ Pr & 4.04 & 2.3$
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$ \begin{array}{ccccc} Cu & 5.32 & 0.58 & 0.44 & 0.91 & 0.59 & 0.66 & 12.36 & 70.39 & 44.24 & 50.69 & 74.22 & 22.47 \\ Zh & 14.84 & 6.82 & 33.68 & 17.84 & 10.27 & 12.93 & 20.34 & 70.22 & 41.64 & 56.98 & 71.46 & 18.68 \\ Rb & 1.20 & 0.69 & 0.73 & 0.69 & 0.43 & 0.66 & 3.46 & 5.72 & 0.93 & 29.74 & 22.47 & 23.10 \\ Sr & 85.14 & 86.27 & 44.48 & 30.90 & 20.32 & 19.74 & 974.53 & 710.27 & 474.38 & 638.87 & 658.66 & 420.14 \\ Ba & 14.78 & 11.15 & 6.49 & 51.2 & 0.47 & 3.43 & 46.92 & 115.24 & 22.20 & 654.05 & 456.22 & 502.44 \\ Zr & 17.22 & 8.75 & 15.03 & 14.98 & 11.18 & 18.63 & 15.16 & 39.16 & 33.75 & 43.80 & 50.38 & 26.37 \\ Hf & 0.32 & 0.11 & 0.31 & 0.27 & 0.10 & 0.40 & 0.40 & 1.10 & 10.11 & 1.34 & 1.51 & 0.75 \\ Ta & 0.04 & 0.02 & 0.04 & 0.03 & 0.05 & 0.04 & 0.07 & 0.13 & 0.07 & 0.12 & 0.15 & 0.09 \\ Pb & 7.34 & 1.04 & 2.22 & 3.56 & 2.66 & 5.17 & 2.94 & 11.82 & 42.3 & 8.85 & 12.03 & 4.37 \\ Th & 5.54 & 2.41 & 2.48 & 3.34 & 1.44 & 3.33 & 0.70 & 2.07 & 1.05 & 1.98 & 2.44 & 1.00 \\ La & 16.50 & 9.96 & 19.70 & 19.23 & 11.22 & 17.11 & 13.34 & 7.66 & 6.75 & 8.03 & 9.72 & 2.44 \\ Ce & 112.53 & 70.32 & 121.36 & 128.87 & 64.30 & 105.46 & 23.55 & 18.82 & 14.18 & 17.01 & 19.93 & 4.76 \\ Pr & 4.04 & 2.32 & 4.23 & 4.25 & 2.43 & 3.74 & 2.68 & 2.10 & 1.70 & 2.02 & 2.38 & 0.70 \\ Nd & 18.79 & 10.02 & 17.48 & 18.10 & 9.95 & 15.94 & 11.16 & 9.04 & 7.45 & 8.67 & 10.13 & 3.17 \\ Sm & 4.41 & 2.03 & 3.52 & 3.93 & 2.10 & 3.43 & 2.01 & 2.16 & 1.73 & 1.99 & 2.25 & 0.84 \\ Ca & 4.99 & 0.03 & 0.52 & 0.57 & 3.51 & 2.04 & 2.49 & 1.90 & 0.22 & 2.38 & 0.70 \\ Nd & 18.79 & 10.02 & 17.48 & 18.10 & 9.95 & 15.94 & 11.16 & 9.04 & 7.45 & 8.67 & 10.13 & 3.17 \\ Sm & 4.41 & 2.03 & 3.52 & 3.93 & 2.10 & 3.43 & 2.01 & 2.16 & 1.73 & 1.99 & 2.25 & 0.84 \\ Ca & 4.99 & 0.03 & 0.62 & 0.74 & 0.43 & 0.58 & 0.33 & 0.43 & 0.34 & 0.40 & 0.44 & 0.21 \\ Dy & 4.87 & 1.73 & 3.72 & 4.11 & 2.42 & 3.36 & 1.92 & 2.60 & 2.11 & 2.38 & 0.76 \\ Ch & 4.99 & 0.03 & 0.02 & 0.01 & 0.04 & 0.43 & 0.58 & 0.47 & 0.53 & 0.61 & 0.31 \\ Fr & 2.84 & 0.92 & 2.26 & 2.02 & 1.24 & 1.71 & 1.15 & 1.57 & 1.41 & 1.54 & 1.69 & 0.90 $
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Mn)
Mg/Ca 0.64 0.43 2.24 1.73 1.55 5.11 0.03 0.14 0.20 0.18 0.34 0.25
Mn/Sr 4907.5 4820.3 9193.3 13788.9 21918.3 21025.5 1.75 1.64 14.53 10.91 22.11 15.30 RFE+Y 195.08 108.57 197.28 204.87 110.33 171.33 73.66 64.85 53.42 61.82 71.49 26.15
Y/Ho 19.42 20.31 19.49 18.77 22.78 19.82 30.58 25.84 27.29 27.16 26.65 28.73
$\mu_{\nu}/\mu_{\nu}^{*}$ 0.78 1.00 1.22 1.01 1.18 0.70 1.09 1.14 1.49 1.50 1.36 1.72 $\gamma_{\nu}/\gamma_{\star}^{*}$ 0.72 0.73 0.67 0.81 0.71 1.16 0.97 1.03 1.02 1.00 1.11
$Ce/Ce^*$ 374 3.77 3.42 3.73 3.14 3.47 1.06 1.11 1.06 1.05 1.03 0.90
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La/Th 2.98 4.13 7.93 5.76 7.80 5.14 19.08 3.70 6.40 4.05 3.98 2.45 Tb/Cs 1.26 1.25 0.62 1.12 0.62 1.02 0.12 0.13 0.05 0.15 0.14 0.09
Sample no. AET2-14 AET2-13 AET2-12 AET2-11 AET2-9 AET2-8 AET2-5 AET2-3 AET2-2 AET2-1 AET1-2 AET1-1
Lithology S. lime. S. lime. S. lime. A. lime. A. lime. A. lime. S. lime. Marl. S. lime. S. lime. Calca. Calca.
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Table 1. Cont.

Sample No.	<b>AET3-7</b>	AET3-8	AET3-9	AET3-10	AET3-11	AET3-12	AET3-16	AET3-14	AET3-6	AET3-3	AET3-2	AET2-16
Be	0.58	0.27	0.26	0.35	0.21	0.21	0.28	0.25	0.21	0.31	0.16	0.15
Sc	15.05	22.14	25.56	14.97	7.73	7.45	22.42	15.86	17.69	17.41	25.50	23.53
V	95.74	140.79	140.55	111.32	66.83	61.57	130.85	82.66	105.29	91.11	133.83	119.89
Cr	57.55	247.80	250.47	108.71	39.45	39.14	168.04	98.32	182.23	55.78	387.12	298.49
Co	11.25	28.07	22.17	17.31	7.91	7.47	17.80	15.56	17.73	15.47	29.28	24.21
Ni	25.77	51.14	75.35	33.16	21.50	20.20	30.47	43.14	39.81	31.83	91.05	75.25
Cu	29.87	55.76	57.52	36.94	21.80	20.72	43.22	24.88	44.87	33.13	48.52	42.02
Zn	51.48	39.20	49.80	43.65	26.17	25.92	49.43	51.62	34.20	43.86	41.52	39.08
Rb	13.24	11.62	8.95	12.23	0.88	0.86	23.12	25.20	3.13	2.47	8.05	5.49
Sr	900.27	966.51	993.82	995.57	1537.85	1378.29	930.55	885.21	949.44	976.66	731.82	773.59
Ba	459.93	334.72	191.17	307.63	30.43	27.16	581.60	611.15	61.38	78.61	335.81	304.35
Zr	45.06	20.06	25.59	34.40	23.18	22.40	30.80	30.84	14.92	44.81	13.31	14.70
Ht	1.41	0.63	0.76	1.02	0.63	0.62	0.95	0.93	0.47	1.33	0.43	0.47
la	0.13	0.05	0.02	0.07	0.05	0.05	0.05	0.06	0.05	0.07	0.04	0.05
Pb	6.72	2.50	1.98	4.24	2.71	3.56	1.23	4.15	3.01	2.22	2.46	2.47
Ih	1.69	0.61	0.74	0.72	0.49	0.46	0.50	0.48	0.60	0.57	0.42	0.45
U	3.21	0.45	0.67	1.46	2.83	2.76	2.79	0.43	1.17	2.02	1.09	1.14
La	8.66	4.59	4.25	3.99	5.63	5.43	4.23	3.74	3.47	5.90	5.09	2.97
Ce	14.33	7.93	8.40	7.16	8.37	7.93	7.87	6.06	5.85	11.30	7.63	4.62
Pr	1.95	1.08	1.08	1.13	1.25	1.19	1.17	0.97	0.84	1.59	1.13	0.74
INd Crea	8.29	4.92	4.82	5.22	5.48	5.26	5.51	4.40	3.69	7.49	4.76	3.30
Sm	1.88	1.21	1.20	1.39	1.26	1.20	1.41	1.16	0.90	1.87	1.09	0.87
Eu	0.60	0.40	0.41	0.44	0.31	0.29	0.47	0.46	0.25	0.51	0.32	0.29
Ga Th	2.21	1.21	1.56	1.51	1.51	1.20	1.67	1.20	0.97	2.27	1.15	0.95
1D Du	0.39	0.22	0.24	0.29	0.24	0.25	0.30	0.25	0.18	0.42	0.20	0.18
Dy	2.44	1.39	1.52	1.07	0.71	0.24	2.05	1.00	1.09	2.33	1.20	1.12
I Llo	16.20	0.00	9.56	10.98	9.71	9.24	12.05	9.55	0.00	16.04	7.67	0.09
Fr.	1.57	1.07	1.00	1.28	1.01	0.32	1.32	1.08	0.23	1.69	0.29	0.20
Tm	0.22	0.16	0.14	0.19	0.14	0.95	0.18	0.16	0.74	0.22	0.07	0.17
Vh	1.54	1 16	1.06	1.35	1.02	0.15	1.24	1 10	0.11	1.58	0.13	0.12
In	0.24	0.19	0.16	0.21	0.16	0.16	0.20	0.19	0.01	0.25	0.12	0.14
$\Delta l_{0}O_{0}/T_{0}O_{0}$	24.67	29.63	29.30	26.82	26.22	25.68	28.80	29.97	33.26	25.68	38.92	28.88
Fe/Ti	19.32	24.14	21.61	17.75	19.64	17 75	18 26	18.09	25.11	14.09	35.79	30.58
$\Delta 1/(\Delta 1 \pm E_0 \pm$	17.52	24.14	21.01	17.75	17.04	17.75	10.20	10.07	20.11	14.07	55.7 5	50.50
Mn)	0.51	0.47	0.45	0.55	0.53	0.55	0.57	0.59	0.53	0.61	0.48	0.45
Mg/Ca	0.20	0.22	0.12	0.12	0.05	0.05	0.21	0.22	0.29	0.08	0.37	0.30
Mn/Sr	5.08	10.10	19.56	2.57	0.60	0.79	1.75	1.22	1 79	0.63	1 48	1.50
REE+Y	61.08	34.72	35.37	37.46	37.69	35.98	40.11	32.24	26.07	54.25	32.63	24.07
Y/Ho	29.44	25.25	26.82	25.14	28.43	28.51	25.40	24 92	27 42	26.99	26.27	26.19
Eu/Eu*	1 40	1.51	1.52	1 40	1 12	1 12	1 43	1 73	1.26	1 17	1.37	1 49
$Y/Y^*$	1 11	1 01	1.02	0.97	1 10	1.09	0.97	0.96	1.04	1.04	1.01	1 01
Ce/Ce*	0.90	0.96	1.01	0.84	0.85	0.85	0.92	0.82	0.88	0.97	0.82	0.81
Nd/YbN	0.45	0.35	0.38	0.32	0.45	0.44	0.37	0.31	0.38	0.39	0.43	0.32
La/Sc	0.58	0.21	0.17	0.27	0.73	0.73	0.19	0.24	0.20	0.34	0.20	0.13
La/Th	5.12	7.47	5.72	5.56	11.41	11.82	8.49	7.80	5.81	10.40	12.04	6.64
Th/Sc	0.11	0.03	0.03	0.05	0.06	0.06	0.02	0.03	0.03	0.03	0.02	0.02
,										0.00		

Abbreviations: A. limestone = argillaceous limestone, S. limestone = sandy limestone, Marl. = marlstone, Calca. = calcarenite. Note:  $Eu/Eu^* = [Eu/(0.67Sm + 0.33Tb)]_{PAAS}$ ;  $Ce/Ce^* = [Ce/(Pr2/Nd)]_{PAAS}$ ;  $Y/Y^* = [2Y/(Dy + Ho)]_{PAAS}$ .

With the exception of some metals, such as V (mean = 85.22 ppm), Cr (mean = 49.96 ppm), and Sr (mean = 47.81 ppm), most trace elements in the Mn(II) carbonate ores are present in low concentrations (<20 ppm; AET3-9 has 33.68 ppm of Zn, while AET3-7 and AET3-12 have 26.30 and 24.61 ppm Ni, respectively; Table 1). The incompatible elements Hf, Th, Sc, and Zr have average concentrations of 0.25, 3.09, 3.09, and 14.30 ppm, respectively. Most of the non-mineralized wall-rock samples of the Kalaatehe Formation have higher transition metal concentrations (e.g., V and Cr >100 ppm, Ni, Cu, and Zn >20 ppm), as well as incompatible elements (e.g., Sc >10 ppm and Zr >20 ppm) than the Mn(II) carbonate ores (Table 1). The non-mineralized rocks are also marked by higher Sr contents, ranging from 420 to 1538 ppm.

The Mn(II) carbonate ores and associated rocks show significant differences in their REE+Y concentrations (Table 1), as well as their PAAS-normalized patterns (Figure 4). The samples of Mn(II) carbonate ores are relatively rich in REE+Y (109–205 ppm). The REE+Y distribution deviates, however, from that of PAAS by displaying positive Ce anomalies (Ce/Ce\*<sub>PAAS</sub> =  $3.55 \pm 0.23$ ) and negative Y anomalies (Y/Y\*<sub>PAAS</sub> =  $0.73 \pm 0.04$ ). No fractionation between light and heavy REE (Nd/Yb<sub>PAAS</sub> =  $0.87 \pm 0.17$ ) is apparent (Figure 4). Moreover, all analyzed Mn(II) carbonate ores have subchondritic Y/Ho ratios ranging from 18.77 to 22.78, far below that of seawater (>36) but within the chemical signal of Mn oxides, in which Y/Ho ratios typically fall below 25 [76]. Generally, the REE+Y concentrations of the non-mineralized wall rocks (24.07–73.66 ppm) are lower than those of the Mn(II) carbonate ores. The PAAS-normalized REE+Y patterns of these non-mineralized rock samples are relatively uniform, with distinct light REE depletion (Nd/Yb<sub>PAAS</sub> =  $0.42 \pm 0.12$ ), consistent positive Eu (Eu/Eu\*<sub>PAAS</sub> =  $1.38 \pm 0.19$ ) anomalies, no meaningful Y (Y/Y\*<sub>PAAS</sub> =  $1.03 \pm 0.06$ )



**Figure 4.** Post-Archean Average Shale (PAAS)-normalized REE+Y distributions of the Ortokarnash Mn(II) carbonate ores and associated wall rocks. Note that, for comparison, those of different origins of marine ferromanganese deposits [76,77], high-temperature (T) hydrothermal fluid [78], and South Pacific deep water [79] are also plotted whole rocks. PAAS data from [80].

# 4.2. Strontium and Neodymium Isotopes

The Sr and Nd isotope results and calculated Nd-depleted mantle model ages (T<sub>DM</sub>) and two-stage Nd model ages (T<sub>2DM</sub>) for Mn(II) carbonate ores and associated wall-rock samples of the Kalaatehe Formation are shown in Table 2. The initial <sup>87</sup>Sr/<sup>86</sup>Sr ratios were calculated using an age of 320 Ma (the approximate depositional age of the Kalaatehe Formation [73]), where <sup>87</sup>Rb/<sup>86</sup>Sr = Rb(ppm)/Sr(ppm) × Natural abundance of <sup>87</sup>Rb/<sup>86</sup>Sr × atomic weight of Sr/Rb, then (<sup>87</sup>Sr/<sup>86</sup>Sr)<sub>i</sub> = <sup>87</sup>Sr/<sup>86</sup>Sr<sub>measured</sub> – (e<sup> $\lambda$ t</sup> – 1) × <sup>87</sup>Rb/<sup>86</sup>Sr. The  $\epsilon$ Nd(t) values were calculated also using the approximate depositional age of 320 Ma, where <sup>147</sup>Sm/<sup>144</sup>Nd = Sm(ppm)/Nd(ppm) × Natural abundance of <sup>147</sup>Sm/<sup>144</sup>Nd × atomic weight of Nd/Sm, then <sup>143</sup>Nd/<sup>144</sup>Nd<sub>(t=320Ma)</sub> = <sup>143</sup>Nd/<sup>144</sup>Nd<sub>(t=320Ma)</sub> / <sup>143</sup>Nd/<sup>144</sup>Nd<sub>CHUR(t=320Ma)</sub> – 1) × 10,000, where CHUR is the <sup>143</sup>Nd/<sup>144</sup>Nd ratio of the chondritic undifferentiated reservoir at the time of interest.

Table 2. Sr-Nd isotopic data of the Mn ores and associated wall rocks of the Upper Carboniferous Kalaatehe Formation.															
Sample No.	Rb	Sr	<sup>87</sup> Rb/ <sup>86</sup> Sr	<sup>87</sup> Sr/ <sup>86</sup> Sr	$\pm 2\sigma$	( <sup>87</sup> Sr/ <sup>86</sup> Sr)i	Sm	Nd	<sup>147</sup> Sm/ <sup>144Nd</sup>	<sup>143</sup> Nd/ <sup>144</sup> Nd	$\pm 2\sigma$	T <sub>DM</sub> (Ga)	T <sub>2DM</sub> (Ga)	εNd(t)	f <sub>Sm/Nd</sub>
AET3-7	1.203	85.145	0.0409	0.707769	0.000013	0.707583	4.406	18.787	0.1418	0.512184	0.000010	2.04	1.62	-6.62	-0.28
AET3-8	0.694	86.267	0.0233	0.707790	0.000013	0.707684	2.028	10.021	0.1223	0.512162	0.000007	1.65	1.59	-6.25	-0.38
AET3-9	0.734	44.480	0.0477	0.707785	0.000013	0.707567	3.522	17.480	0.1218	0.512165	0.000009	1.63	1.58	-6.17	-0.38
AET3-10	0.694	30.904	0.0650	0.707812	0.000014	0.707516	3.931	18.100	0.1313	0.512188	0.000010	1.78	1.58	-6.11	-0.33
AET3-11	0.434	20.316	0.0618	0.707816	0.000012	0.707535	2.096	9.954	0.1273	0.512190	0.000010	1.69	1.56	-5.91	-0.35
AET3-12	0.658	19.743	0.0965	0.708953	0.000013	0.708513	3.431	15.941	0.1301	0.512185	0.000010	1.76	1.58	-6.12	-0.34
AET3-16	3.457	974.534	0.0103	0.707806	0.000013	0.707759	2.012	11.156	0.1090	0.512278	0.000011	1.27	1.36	-3.44	-0.45
AET3-14	5.722	710.266	0.0233	0.707656	0.000013	0.707550	2.162	9.042	0.1446	0.512438	0.000011	1.57	1.22	-1.77	-0.27
AET3-6	0.926	474.381	0.0057	0.707608	0.000012	0.707582	1.730	7.454	0.1403	0.512562	0.000011	1.22	1.01	0.82	-0.29
AET3-3	29.742	638.867	0.1347	0.708026	0.000009	0.707412	1.987	8.672	0.1385	0.512434	0.000010	1.45	1.21	-1.60	-0.30
AET3-2	22.469	658.656	0.0987	0.707934	0.000011	0.707484	2.250	10.131	0.1342	0.512425	0.000009	1.39	1.21	-1.60	-0.32
AET2-16	23.099	420.144	0.1591	0.708230	0.000013	0.707505	0.844	3.174	0.1607	0.512545	0.000010	1.74	1.11	-0.34	-0.18
AET2-14	13.242	900.273	0.0426	0.707726	0.000011	0.707532	1.879	8.286	0.1371	0.512496	0.000010	1.30	1.11	-0.33	-0.30
AET2-13	11.616	966.506	0.0348	0.707767	0.000012	0.707608	1.206	4.922	0.1481	0.512750	0.000011	0.93	0.74	4.18	-0.25
AET2-12	8.949	993.815	0.0261	0.707676	0.000014	0.707557	1.203	4.815	0.1511	0.512686	0.000011	1.13	0.85	2.80	-0.23
AET2-11	12.227	995.568	0.0355	0.707774	0.000012	0.707612	1.393	5.220	0.1613	0.512664	0.000008	1.42	0.92	1.96	-0.18
AET2-9	0.883	1537.854	0.0017	0.707720	0.000014	0.707712	1.262	5.482	0.1392	0.512463	0.000009	1.41	1.17	-1.07	-0.29
AET2-8	0.861	1378.290	0.0018	0.707628	0.000013	0.707620	1.205	5.257	0.1386	0.512476	0.000010	1.37	1.14	-0.78	-0.30
AET2-5	23.120	930.546	0.0719	0.707744	0.000014	0.707416	1.413	5.514	0.1549	0.512703	0.000010	1.16	0.84	2.98	-0.21
AET2-3	25.205	885.214	0.0824	0.707842	0.000012	0.707467	1.156	4.401	0.1588	0.512718	0.000008	1.20	0.83	3.11	-0.19
AET2-2	3.130	949.438	0.0095	0.707756	0.000013	0.707712	0.897	3.689	0.1470	0.512589	0.000010	1.28	0.99	1.08	-0.25
AET2-1	2.470	976.658	0.0073	0.707686	0.000011	0.707652	1.870	7.486	0.1510	0.512677	0.000011	1.15	0.87	2.63	-0.23
AET1-2	8.048	731.819	0.0318	0.707588	0.000015	0.707443	1.088	4.759	0.1382	0.512610	0.000012	1.09	0.93	1.85	-0.30
AET1-1	5,494	773.594	0.0205	0.707796	0.000013	0.707702	0.874	3.305	0.1600	0.512627	0.000010	1.49	0.98	1.29	-0.19

For the six analyzed Mn(II) carbonate ores, the Rb and Sr contents vary from 0.43 to 1.20 ppm and from 19.74 to 86.27 ppm, respectively, while the  $^{87}$ Rb/ $^{86}$ Sr and  $^{87}$ Sr/ $^{86}$ Sr ratios have limited ranges between 0.0233 and 0.0965, and between 0.707769 and 0.708953, respectively. The ( $^{87}$ Sr/ $^{86}$ Sr)<sub>i</sub> ratios of Mn(II) carbonate ores are relatively uniform, varying from 0.707516 to 0.707684 (mean of 0.707577  $\pm$  0.000058), and the AET3-12 sample has a relatively high ( $^{87}$ Sr/ $^{86}$ Sr)<sub>i</sub> ratio of 0.708513. The samarium and Nd contents of the analyzed Mn(II) carbonate ores vary from 2.03 to 4.41 ppm and from 9.95 to 18.79 ppm, respectively. The  $^{147}$ Sm/ $^{144}$ Nd ratios fall in the range of 0.1218–0.1418, with a mean of 0.1291, and the  $^{143}$ Nd/ $^{144}$ Nd ratios are relatively uniform, defining an average subchondritic value of 0.512179  $\pm$  0.000011. The Nd model ages (T<sub>2DM</sub>) range from 1.56 to 1.62 Ga (mean of 1.58  $\pm$  0.02 Ga). There are no large variations in the  $\epsilon$ Nd(t) values (from –6.64 to –5.92, mean of –6.20  $\pm$  0.21).

In terms of the non-mineralized rocks, these samples are characterized by relatively low Rb (0.86–29.74 ppm) and high Sr (420.1–1537.9 ppm) contents. Consequently, the <sup>87</sup>Rb/<sup>86</sup>Sr and <sup>87</sup>Sr/<sup>86</sup>Sr ratios have slightly large variations, ranging from 0.0017 to 0.1591 and from 0.707588 to 0.708230, respectively. In contrast, the  $({}^{87}Sr)/{}^{86}Sr)_i$  ratios of these nonmineralized rocks are relatively uniform, defining an average value of  $0.707574 \pm 0.000104$ (0.707412–0.707759). The samarium and Nd contents of these associated wall rocks range from 0.84 to 2.25 ppm and from 3.17 to 11.16 ppm, respectively. The  $^{147}$ Sm/ $^{144}$ Nd and  $^{143}$ Nd/ $^{144}$ Nd ratios in these non-mineralized rock samples vary between 0.1090 and 0.1613, and between 0.512278 and 0.512750, respectively. However, the ɛNd(t) values of these wall-rock samples are different (Table 2). For example, two calcarenite samples of the first member have  $\varepsilon Nd(t)$  values of 1.29 and 1.85, respectively. The sandy limestone samples of the second member have positive  $\varepsilon Nd(t)$  values varying from 1.08 to 4.18, with the exception that sample AET2-14 has a negative  $\varepsilon Nd(t)$  value of -0.33 (Table 2). In contrast, negative  $\varepsilon$ Nd(t) values are dominated in the marlstone samples of the third member, with the  $\varepsilon$ Nd(t) values ranging from –1.77 to –0.34 (AET2-3 have a positive  $\varepsilon$ Nd(t) value of 3.11; Table 2). In addition, these non-mineralized rocks yield T<sub>2DM</sub> model ages between 0.74 and 1.36 Ga.

#### 5. Discussion

## 5.1. Evaluation of Detrital Contamination and Alteration

Generally, non-carbonate components (e.g., siliciclastic materials) presented in sediments and sedimentary rocks play an important role in controlling the Sr and Nd isotope budget (e.g., [81–87]). Petrographic observation (Figure 3) and major element analyses (Table 1) indicate that the Upper Carboniferous Kalaatehe Formation, especially the nonmineralized wall rocks, are generally not pure carbonates but mixed carbonate–siliciclastic rocks. Therefore, it is necessary to evaluate such potential effects.

With respect to the Mn(II) carbonate ores, a positive correlation occurred between the  $({}^{87}\text{Sr}/{}^{86}\text{Sr})_i$  and Al<sub>2</sub>O<sub>3</sub> (R<sup>2</sup> = 0.52; Figure 5A). It is noteworthy, however, that this linear relationship is mainly controlled by one outlier point (AET3-12), which has the highest Al<sub>2</sub>O<sub>3</sub> content and the highest initial  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$  value. This is indicative of significant Alrich clastic components in controlling the initial  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$  value of the AET3-12 sample. Alternatively, the other five Mn(II) carbonate ores had relatively uniform initial  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$  values (0.707516–0.707684), although the Al<sub>2</sub>O<sub>3</sub> contents in these samples are variable (Figure 5A), indicating that the detrital contamination on the Sr isotopic composition is negligible. In addition, there is no meaningful correlation between  $\epsilon$ Nd(t) and Al<sub>2</sub>O<sub>3</sub> (R<sup>2</sup> = 0.05; Figure 5B), arguing for a negligible influence of detrital contamination on Nd isotopes in these Mn(II) carbonate ores.



**Figure 5.** Cross-plots of (**A**)  $({}^{87}\text{Sr}/{}^{86}\text{Sr})_i$  and (**B**)  $\epsilon$ Nd(t) vs. Al<sub>2</sub>O<sub>3</sub> content for the Ortokarnash Mn(II) carbonate ores.

In terms of non-mineralized wall rocks, the presence of a negative co-variation between  $Al_2O_3$  and CaO ( $R^2 = 0.80$ ; not shown) is indicative of two dominant compositional end-members (i.e., siliciclastic material and carbonate) of the Kalaatehe Formation. However, the much higher Sr content than in the upper continent crust (e.g., shale; Figure 6A), in combination with the positive correlation between Sr and CaO ( $R^2 = 0.79$ ; not shown), demonstrates a large amount of Sr, likely resulting from the substitution of  $Ca^{2+}$  for Sr<sup>2+</sup> during the carbonate formation. Therefore, chemical carbonate precipitates likely play an important role in controlling the Sr isotope compositions. However, the presence of a remarkable linear relationship between (<sup>87</sup>Sr/<sup>86</sup>Sr)<sub>i</sub> and Al<sub>2</sub>O<sub>3</sub> for these marlstone  $(R^2 = 0.99)$  as well as these argillaceous limestone samples  $(R^2 = 0.73;$  Figure 6B) indicates that Al-rich clastic components (e.g., volcanoclastic material) were important in affecting the initial <sup>87</sup>Sr/<sup>86</sup>Sr ratios, although this potential effect may be less significant in those sandy limestone samples. Moreover, a broad trend showing lower initial <sup>87</sup>Sr/<sup>86</sup>Sr ratios with increasing Al<sub>2</sub>O<sub>3</sub> contents is, to some extent, presented in all these non-mineralized wall rocks (Figure 6B), indicating that the terrestrial debris is characterized by a low initial <sup>87</sup>Sr/<sup>86</sup>Sr ratio. Considering that the Lower Carboniferous Wuluate Formation in the Malkansu district mainly consists of basalts that have (<sup>87</sup>Sr/<sup>86</sup>Sr)<sub>i</sub> values of 0.705624–0.707962 [71], the contamination of these volcanoclastic debris likely results in more nonradiogenic Sr.



**Figure 6.** Cross-plots of Al<sub>2</sub>O<sub>3</sub> vs. (**A**) Sr content, (**B**)  $({}^{87}\text{Sr}/{}^{86}\text{Sr})_i$ , (**C**) Nd content, and (**D**)  $\varepsilon$ Nd(t) for the associated wall rocks of the Ortokarnash manganese ore deposit.

Although the Nd contents in these sandy limestone and marlstone samples are relatively higher than that of the upper continental crust, there is a distinct positive correlation between the  $Al_2O_3$  and Nd contents ( $R^2 = 0.92$ ) in these argillaceous limestone samples, which is indicative of a contribution from the Al-rich clastic components (Figure 6C). However, this terrigenous contribution to the Nd content may not be transferred to the corresponding Nd isotopic composition. It is noteworthy that no meaningful correlation occurred between the  $Al_2O_3$  and  $\epsilon$ Nd(t) values in these non-mineralized samples (Figure 6D), suggesting that this potential contamination effect is not significant in these rocks (e.g., marlstone and sandy limestone).

Carbonate rocks are particularly vulnerable to multiple stages and styles of postdepositional diagenetic alteration, which, to some extent, likely exerts significant influence on the isotope compositions (e.g., C, O, and Sr isotope) [88–92]. Previous studies have suggested that the Ortokarnash Mn(II) carbonate ores are the products resulting from the reduction of precursor Mn(III/IV) oxide precipitates in the presence of organic matter during early diagenesis [44,73]. Considering that Mn(III/IV) oxides are depleted in Sr, Ca, and Mg (e.g., [93]), these elements in Mn(II) carbonate ores (Figure 3F) were likely derived from pore waters during late diagenesis. Therefore, the Sr isotopes in these Mn(II) carbonate ores likely reflect the isotopic features of the pore water.

In contrast to Sr, REEs are immobile and thus, relatively unsusceptible to diagenesis [80,94,95]. This hypothesis is further supported by the PAAS-normalized REE patterns, which show characteristics of modern submarine hydrogenetic Fe-Mn deposits (Figure 4), suggesting that the Mn(II) carbonate ores inherited the REE features of primary Mn(III/IV) oxide precipitates [44]. Consequently, it is expected that the Nd isotopes in these Mn(II) carbonate ores also likely inherited those of primary Mn(III/IV) oxides. Moreover, the  $T_{2DM(Nd)}$  ages for these Mn(II) carbonate ores range from 1.63 to 2.04 Ga and from 1.56 to 1.62 Ga (Table 2), respectively, which are remarkably older than their depositional age (~320 Ma). These collectively suggest that the Nd isotope composition of the Mn(II) carbonate ores was not altered during post-depositional processes.

Conventionally, high Sr contents and low Mn/Sr ratios are characteristics of carbonate sediments with minimal influence by meteoric diagenesis (e.g., [88,89,96–98]). Based on petrographic observations, most samples analyzed in this study are sandy limestone with micritic carbonate grains and marlstone with dominantly micritic matrix and muds. Generally, recrystallization was more or less visible under the microscope, though no remarkable dolomitization was observed (Figure 3B,D). In the Kalaatehe Formation, the Sr contents of non-mineralized rocks vary from 420 ppm to 1538 ppm, with a mean of 883 ppm, and the Mn/Sr ratios vary from 0.60 to 22.11 (mean of 6.29). It is noteworthy, however, that the samples directly either underlying or overlying the Mn(II) carbonate ore zone possess relatively high Mn/Sr ratios (5.08–22.11, mean of 13.94) (Table 1), suggesting a close relationship with Mn ore layers [44]. In addition, all analyzed non-mineralized rock samples are characterized by low Mg/Ca ratios ranging between 0.03 and 0.37 ( $0.18 \pm 0.10$ ). This means that the non-mineralized rocks are independent of dolomitization (e.g., [99,100]). Moreover, no correlations between the (<sup>87</sup>Sr/<sup>86</sup>Sr)<sub>i</sub> and Mn/Sr and between the (<sup>87</sup>Sr/<sup>86</sup>Sr)<sub>i</sub> and Mg/Ca ratios were found in these wall rocks ( $R^2 = 0.12$  and 0.08, respectively; Figure 7A,B). Accordingly, it is unlikely that interactions with meteoric or burial fluids have significantly altered the Sr isotopes.



**Figure 7.** Cross-plots of  $({}^{87}\text{Sr}/{}^{86}\text{Sr})_i$  vs. (A)  $(Mn/Sr)_{auth.}$  and (B)  $(Mg/Ca)_{auth.}$  for the associated wall rocks of the Ortokarnash Mn ore deposit.

The  $T_{DM(Nd)}$  and  $T_{2DM(Nd)}$  ages for these non-mineralized wall rocks range from 0.93 to 1.74 Ga and from 0.74 to 1.36 Ga (Table 2), respectively, which are obviously older than their depositional age (~ 320 Ma). Furthermore, all Sm–Nd isotope data of associated wall rocks are plotted along a correlation line in a conventional isochron diagram (not shown), with an apparent age of 1361 ± 510 Ma (MSWD = 3.3) and an initial <sup>143</sup>Nd/<sup>144</sup>Nd value of 0.51127 ± 0.00049, suggesting that all the non-mineralized wall rocks in the studied section have remained closed with respect to Sm–Nd isotopes since shortly after deposition/formation.

#### 5.2. Inference for Provenance of Terrigenous Input

As described above, high and variable concentrations of Al<sub>2</sub>O<sub>3</sub> (4.72–11.78) (Table 1) and high modal contents of volcanic debris and silicate mineral (e.g., pyroxene and feldspar)

(Figure 3A,B,D) in the non-mineralized wall rocks suggest a significant detrital input. To discriminate the source of these detrital contaminants, immobile element pairs can be used [101]. It is generally accepted that Al and Ti do not fractionate during weathering, transportation, and deposition [102,103]. The Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> ratios of non-mineralized wall rocks vary from 24.67 to 38.92, with a mean of 28.64. These values are comparable with those of the WKOB mafic volcanics (17.99–36.61, mean of 23.48 [41,71]) but are significantly lower than that of the felsic volcanics (27.64–91.94, mean of 47.99 [104,105]). Incompatible to compatible element ratios, such as La/Sc and Th/Sc, are radically different mafic and felsic materials that have been proven to be useful tools for discriminating the provenance of sedimentary rocks [106,107]. The La/Sc and Th/Sc ratios of the non-mineralized wall rocks range from 0.13 to 0.73 (AET3-16 has La/Sc ratio of 2.39) and from 0.02 to 0.15, respectively (Table 1). These values contrast markedly with those for felsic sources (La/Sc and Th/Sc ratios of 2.50–16.3 and 0.84–20.5, respectively) but are similar to those of mafic sources (0.43–0.86 and 0.05–0.22, respectively [108]), indicating significant contributions from the mafic rocks. Moreover, on the diagram of La/Th vs. Hf (Figure 8A), all data of the non-mineralized wall rocks are plotted in or close to the basic field, which is mainly indicative of mafic sources [109,110]. These examples above imply again that mafic rocks (e.g., basalts of the Upper Carboniferous Wuluate Formation) were an important component of the provenance.



**Figure 8.** (**A**). Source rock discriminating diagrams for the non-mineralized wall-rock samples on La/Th vs. Hf (modified after [109]). Average reference compositions are from [111]. (**B**).  $\varepsilon$ Nd(320 Ma) vs. Th/Sc diagrams of the non-mineralized wall-rock samples. End member compositions are from [101]. Data sources are from [63,71,104,105].

In addition, radiogenic isotopes in combination with geochemical data can be instrumental in understanding the nature of sediment sources [87,110,112]. It was suggested that sedimentary rocks with relatively low Th/Sc ratios and high  $\varepsilon$ Nd(t) values are likely to be derived from less differentiated, young source terranes, while high Th/Sc ratios and low  $\varepsilon$ Nd(t) values probably indicate an upper crustal source [109,110]. Figure 8B plots the  $\varepsilon$ Nd(t = 320 Ma) values against the Th/Sc ratios. Shown for reference are the location of the typical upper crust, intermediate island arc compositions, and the MORB calculated at the approximate time of deposition (320 Ma). Meanwhile, samples of mafic (basalt and gabbro) and basement rocks in the WKOB [63,71,104,105] are also plotted. Nearly all of the calcarenite and sandy limestone samples of the first and second members have positive  $\varepsilon$ Nd(t) values and relatively low Th/Sc ratios, similar to those of the WKOB basalt, indicating that mafic igneous rocks from either the older or coeval differentiated terrane (likely the Lower Carboniferous basalts of the Wuluate Formation [71]) were the major sources. This is further supported by the presence of a broad trend showing lower initial  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios with increasing Al<sub>2</sub>O<sub>3</sub> contents in all non-mineralized wall rocks (Figure 6B), also arguing for the terrestrial debris sourced from these possible mafic rocks.

# 5.3. Implications for the Mn Source

Generally, terrestrial silicate weathering and submarine hydrothermal activity are conventionally suggested to be the particular source of Mn in ancient deposits (e.g., [2,3]). The Ortokarnash Mn deposits were proposed to form in either a failed rift basin [113] or a back-arc basin [40,44], and the Mn could be sourced from hydrothermal fluids related to the volcanic activity in such a setting. Furthermore, Zhang et al. [44] preferred a hydrothermal source of Mn, given that the presence of many VMS deposits are hosted within the volcanic rocks of the Lower Carboniferous Wuluate Formation in the southeast of the Malkansu manganese metallogenic zone [114], although a lateritic weathering contribution of Mn is still cannot be ruled out [44]. Volcanic debris in the sandy limestone and interbedded tuff layers in the marlstone [41] point towards contemporaneous volcanic activity during the deposition of the Kalaatehe Formation [44]. Moreover, in the discriminant plots of  $SiO_2$  vs.  $Al_2O_3$  (Figure 9A [115]) and Fe/Ti vs. Al/(Al + Fe + Mn) (Figure 9B [116]), proposed to distinguish hydrothermal vs. hydrogenous sources of marine metalliferous sediments, the Ortokarnash Mn(II) carbonate ores fall closer to the hydrothermal endmembers. This is also consistent with some Mn(II) carbonate ore samples displaying weakly positive Eu anomalies (e.g., AET3-9, -10, and -11 have Eu/Eu\* values of 1.25, 1.09, and 1.04, respectively) [78].



**Figure 9.** Discriminant plots of sediments with hydrothermal and hydrogenous origins. (**A**) SiO<sub>2</sub> vs. Al<sub>2</sub>O<sub>3</sub> [115]. Data of average deep-sea sediments are from [117]. (**B**) Fe/Ti vs. Al/(Al + Fe + Mn), and the line shows hydrothermal composition percentages [116]. Data of hydrothermal Fe-Mn deposits are from [76,77].

Because Nd has a larger ionic radius than Sm, Nd is considered more incompatible than Sm. More incompatible elements will be preferentially partitioned into the crust during mantle melting and differentiation, and thus, the continental crust has a lower Sm/Nd ratio than the depleted mantle (e.g., [118,119]). Consequently, ancient continental crust exhibits low (unradiogenic)  $\varepsilon$ Nd(t) values, whereas younger volcanic sequences generally have much higher (radiogenic)  $\varepsilon$ Nd(t) values (e.g., [120]). Studies on global marine Nd isotopic compositions have revealed that the Nd budget of the modern oceans is dominated by dissolved riverine input and by those mobilized from continental erosion products, such as eolian dust and/or continental margin sediments (e.g., [86,121–126]). For instance,

the weathering of young mantle-derived rocks surrounding the Pacific Ocean leads to more radiogenic initial  $\varepsilon$ Nd(0) values compared to those of the Atlantic Ocean, with its margin predominantly composed of old continental crust [127]. Thus, it can be inferred that the Nd isotope features of basin seawater are closely related to local Nd sources. As discussed in Section 5.2, the provenance of syn-depositional detrital contaminants in the non-mineralized wall rocks is dominantly a depleted mafic source. Accordingly, the weathering of these mafic rocks likely results in basin seawater possessing a basalt-like initial  $\varepsilon$ Nd composition (i.e., positive  $\varepsilon$ Nd(t) value), likely representing the terrigenous input to the seawater.

The Nd isotope compositions in Mn(II) carbonate ore samples are less contaminated by terrestrial debris and suffered no post-depositional alteration and, thus, can be used to deduce the chemical properties of seawater. However, the Mn(II) carbonate ores possess negative Nd isotope compositions. This is clearly different from those of terrigenous input above, suggesting another important end-member controlling the Nd isotope composition of Mn ore samples. Given the relevant geochemical features, such as positive Eu anomalies, observed in these samples, we attribute this end-member to hydrothermal fluids percolating and leaching the underlying older continental crust. Interestingly, this idea is similar to the conclusion of [18], who also proposed that the hydrothermally-derived Mn possessed unradiogenic Nd isotopes. Similar examples have been also found in modern submarine hydrothermal systems (e.g., [128–130]. For example, Piepgras and Wasserburg [128] reported Nd isotopic data for a hydrothermal system developed on a sediment-covered ridge in the Guaymas Basin, Gulf of California. The vented hydrothermal fluid (T > 300  $^{\circ}$ C) migrated through a sedimentary package several hundred meters thick. In contrast to solutions from sediment-starved ridges, which show positive Eu anomalies and positive  $\varepsilon$ Nd(t) values [130], this solution possesses similar Eu anomalies but displays negative  $\varepsilon$ Nd (t) values ( $\varepsilon$ Nd(0) = -11.4), indicating that the Nd isotopic signatures of marine fluids are controlled by the compositions of host rocks [85]. Taking these examples into consideration, we propose that REE and manganese were obtained through long-term interaction between hydrothermal fluids and the underlying old continental crust ( $\epsilon Nd(t) < 0$ ) (Figure 10).



**Figure 10.** Schematic diagrams showing a sedimentary model for the Ortokarnash manganese ore deposit in a back-arc basin.

#### 6. Conclusions

The Upper Carboniferous Kalaatehe Formation can be divided into three members, with the first member consisting of limestone containing volcanic breccia, the second member comprised of sandy limestone, and the third member being dark-gray to black marlstone with Mn(II) carbonate layers. Petrographic observations, together with geochemical discrimination proxies, reveal that both the initial <sup>87</sup>Sr/<sup>86</sup>Sr and  $\varepsilon$ Nd(t) compositions of the Mn(II) carbonate ores are not contaminated by continental debris. The Sr isotopes of the

Mn(II) carbonate ore samples are affected by post-depositional alteration, while Nd isotopes remain unaltered. With respect to these associated wall rocks, the Sr isotopic compositions are likely the results of a mixture of the carbonate-rich chemical components (i.e., seawater) and the Al-rich components (e.g., volcanoclastic material), while the potential effects on Nd isotopes are negligible. Both Sr and Nd isotopes in these non-mineralized wall rocks remained unchanged during post-depositional processes. The aluminosilicate fractions in these non-mineralized wall rocks were mainly derived from a depleted mafic source. The REE and possible Mn of the Ortokarnash Mn(II) carbonate ores were derived from seafloor-vented hydrothermal fluids that received their Sm–Nd isotopic signatures through interaction with the underlying old continental crust.

**Author Contributions:** Conceptualization, B.-L.Z., Z.-C.L. and C.-L.W.; methodology, Z.-G.D. and X.Z.; formal analysis, B.-L.Z. and Z.-G.D.; investigation, X.-F.Y., Y.-S.L. and S.-M.Z.; writing—original draft preparation, B.-L.Z.; writing—review and editing, B.-L.Z. and C.-L.W.; supervision, Z.-C.L.; funding acquisition, B.-L.Z. and C.-L.W. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the National Science Foundation of China grants numbers 42102114, U1703242, and by the China Postdoctoral Science Foundation (2021M703018). And C.-L.W. was funded by the Key Research Program of Frontier Sciences, Chinese Academy of Sciences (ZDBS-LY-DQC037), and the Youth Innovation Promotion Association, Chinese Academy of Sciences.

**Acknowledgments:** We would like to thank Zhaozhi Zhong, Lidong He, Bin Zha, Yueqiao Xie, and Zhimin Xie for their support during field work, as well as Chaofeng Li, Wenjun Li, and Bingyu Gao for their assistance in the laboratory.

Conflicts of Interest: The authors declare no conflict of interest.

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