Snowball Earth to global Warming: Coupled vanadium-carbonaceous deposits in the Cryogenian-Cambrian

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ABSTRACT

The anticipated high demand for new vanadium resources in support of the green energy revolution will be partly met by vanadium in carbonaceous deposits. This type of deposit is particularly developed during a 200 Myr period from Cryogenian-Cambrian. During this period, anoxic conditions were widely developed and provided a template for vanadium deposition. Vanadium became available to the surface during the Neoproterozoic when anomalously high levels were introduced in large igneous provinces. Global glacial erosion transported vanadium to the oceans, along with trace elements that engendered organic carbon accumulation. The combination of vanadium and organic carbon gave rise to a range of deposits, and provides a model to support exploration for further resources.

1. Introduction

Green energy requires a step change in the use of minerals. For example, wind energy technology needs a much greater mineral resource than fossil fuel-based technology (International Energy Agency 2022). Battery performance is widely highlighted as a driver for metal and graphite exploration. The vanadium-flow battery is an option to help address the needs of the green energy revolution (Parasuraman et al. 2013, Zhang et al. 2019, Gencten & Sahin 2020). The manufacture of the batteries will require additional resources of vanadium, and hence prompted new exploration and mining projects in many countries (Colthorpe 2021). One of the most promising deposits is the Green Giant vanadium deposit in Madagascar (Scherba et al. 2018). The vanadium deposit is spatially associated with graphite deposits, both of which are licenced by a single exploration company. The association is widely described as serendipitous (Nextsource Materials 2017). However, a review of vanadium deposits in shale sequences shows that the association of vanadium with carbon-rich sediments was well developed in Cryogenian-Cambrian successions, i.e. ~ 700–500 Ma (Fig. 1; Table 1). The widespread occurrence of this association, which had not been evident in the earlier geological record, suggests that the availability of vanadium had markedly increased.

2. The anomalous supply of vanadium

The abundance of vanadium at the Earth’s surface rose distinctly during the Neoproterozoic. Several data sets reflect the trend (Fig. 2). Firstly, the number of distinct vanadium minerals increased sharply (Moore et al. 2020), reflecting both the number of localities where they are recorded and the formation of alteration products following atmospheric oxygenation. Secondly, the V content of marine pyrite increased as the concentration increased in sea water (Mukherjee & Large 2020). Thirdly, the maximum V content of black shales increased, also reflecting sea water composition (Sahoo et al. 2012).

Enrichment of the Neoproterozoic crust in vanadium was heralded by global magmatic activity (Li et al. 2008). Vanadium V$^{3+}$ ions have an ionic radius similar to Fe$^{3+}$ ions, so V commonly substitutes for Fe in magnetite and ferromagnesian silicate minerals formed during magmatism. Consequently, mafic rocks are relatively enriched in V. Following Neoproterozoic magmatism, global Sturtian glaciation at ~ 700 Ma, and younger Neoproterozoic glaciations, enhanced V availability. Glacial erosion contributes much finely ground material into the oceans (Anderson 2007), and the glacial events especially caused extensive deep erosion of vanadium-enriched crust, bringing vanadium to the surface environment just as increasing oxygen levels contributed to its mobility.

An anomalous vanadium enrichment in the magmatic rocks is evident in the detailed chemistry of Neoproterozoic igneous provinces.

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A review of three igneous provinces in which glacial erosion excavated the volcanic rocks and incorporated them into the glacial deposits consistently shows compositions several times the upper continental crust average of 60 ppm V and higher than the basalt average of 250 ppm V (Kelley et al. 2017). The high V contents are also shown by igneous provinces at the end of the Neoproterozoic, which post-dated the glaciations but were eroded into the Cambrian oceans.

Weathering of the Neoproterozoic basalts has been implicated in the drawdown of carbon dioxide and cooling, which prompted the Sturtian glaciation (Lenton et al. 2014, Goddéris et al. 2003, Cox et al. 2016, Donnadieu et al. 2004). The basalts of this magmatic episode would have been highly weatherable (Goddéris et al. 2003, Lenton et al. 2014), and the weathering of an atypically large volume of basalt at that time would have liberated anomalous amounts of vanadium to surface systems. The average basalt has a vanadium content about twelve times that of the average granite (mean values 250 ppm basalt, 20 ppm granite) (Kelley et al. 2017), which would normally have dominated the detritus from eroding continents. Considering the greater susceptibility of basalt to weathering, up to twenty times faster than granitic rocks (Horton 2015), the erosion of typical basaltic terrain might increase the flux of vanadium by two orders of magnitude relative to typical granitic terrain. The contrast would have been even greater in the Neoproterozoic, when basalts contain vanadium levels higher than the average basalt. The model for accelerated weathering is based on basalts on the Laurentian continent (Mills et al. 2014, Donnadieu et al. 2004, Horton 2015), where the Franklin Igneous Province (FIP) covers an area exceeding 2 million km². A direct contribution from FIP basalts is evident in Alaska where they interfinger with glacial diamictite and contribute clasts to it (Macdonald 2011). Several data sets from Alaska to Greenland show mean vanadium levels in the FIP nearly 50% greater than those of average basalts (Fig. 3, Table 2). The weighted mean of the data sets is 351 ppm V (n = 167). These statistics combine to indicate the liberation of vanadium by weathering of the FIP up to 350 times that of granitic terrain, independent of any additional enhancement due to rapid glacial weathering.

The FIP was not the only large igneous province whose rocks were sequestered by Sturtian glaciation (Fig. 4). Neoproterozoic basalts in Australia, including volcanics in the Gairdner Igneous Province, are also V-rich. Seven data sets for basalts all have mean contents well above the mean basalt composition of 250 ppm V, and a weighted mean value of 346 ppm V (n = 61) (Table 2). There is direct evidence for the erosive downcutting of glacial beds into the basalts by the Sturtian glaciation, and the resultant incorporation of basalt clasts in the tillite (Mitchell et al. 2019). Similarly, four data sets for basalts in the Anti-Atlas Supergroup in Morocco have mean contents above 300 ppm V, and a weighted mean value of 321 ppm V (n = 46) (Table 2). Glacial diamictites there have incorporated volcanic clasts (Letsch et al. 2018). Furthermore, neodymium isotope data indicate an enhanced contribution of eroded magmatic rock to marine sediments from about 750 to 600 Ma (Horton 2015), confirming that the potential of this volcanic feedstock was realized.

The high availability of vanadium continued after the glaciations, including for example basalts of the Dalradian Supergroup in Britain and Ireland, and flood basalts of the Volyn Large Igneous Province across Eastern Europe, Belarus and Ukraine. They have weighted mean values of 376 ppm V (n = 43) and 369 ppm V (n = 45) respectively. The continuing supply of vanadium, in the latter part of the Neoproterozoic, was available to surface environments in the Lower Palaeozoic, especially the Cambrian.

Following the delivery of abundant V to the upper crust, availability of the V was facilitated by the higher oxygen content of the atmosphere from the late Neoproterozoic onwards. Increased oxygen allowed greater concentrations of dissolved V in surface waters and seawater (Moore et al. 2020). Prior to the late Neoproterozoic, when oceans were anoxic, levels of dissolved V were relatively low. Then in the late Neoproterozoic V was readily available for incorporation into anoxic sediments.

The combination of repeated mafic volcanism, global glacial erosion, and oxygenation of the atmosphere set the scene for vanadium enrichment of anoxic sea floor sediments.
Carbon-rich sediments were deposited following the late Neo-
proterozoic 'Snowball Earth' glaciations, when the oceans were flooded with fresh nutrients which supported extensive microbial growth (Plana
vsky et al. 2010). The development of anoxia, promoting the preser-
vation of organic carbon, continued through the Cambrian, most notably in the Upper Cambrian Alum Shale in Europe. This period of about 200
million years saw the biggest peak in black shale sedimentation over the last 1500 million years (Condle et al. 2001).

Under anoxic conditions, V was incorporated in carbon-rich sedi-
ments as silicates and associated with organic matter (Breit & Wanty 1991). As carbonaceous rocks are metamorphosed, their clay minerals
are converted to micas, which helps the sequestration of V. The main
residence of V in (meta-)sedimentary rocks is in vanadiferous micas (Fig. 5), often the mineral roscoelite. Accordingly, graphic rocks containing V are commonly characterized by green micas, i.e. roscoelite. The record of V deposits in carbon-rich sediments through Cambrian-Cambrian time shows a range from organic- and clay-hosted V (e.g. Alum Shale; Lerat et al. 2018) to roscoelite-hosted V (e.g. Mozambique), related to the degree of metamorphism. Exceptionally, continued metamorphism in a sequence that also contains meta-evaporites caused expulsion of V from sheet silicates to form vanadiferous garnets (tsavorite) in East Africa (Feneyrol et al. 2013, Giuliani et al. 2018). Tsavorite deposits occur in Neoproterozoic garnitic gneisses in Madagascar, Tanzania and Kenya, accompanied by V-rutile, V-kyanite, V-muscovite, V-zoisite and V-pyr-
rhotite (Giuliani et al. 2018) and Antarctica (Osanai et al. 1990). The tsavorite deposits are not a commercial source of V, but serve to emphasize the strong link between V accumulation and carbon-rich sediments during Cryogenian-Cambrian time. In a further variation in south west Africa, especially Namibia, V-bearing Neoproterozoic rocks were extensively weathered to leave V-mineralized karst during the Paleogene, including what were once among the richest V deposits in the

### Table 1

<table>
<thead>
<tr>
<th>Country</th>
<th>Major vanadium deposit</th>
<th>Formation</th>
<th>Age (Ma)</th>
<th>Organic carbon</th>
<th>V₂O₅ resource</th>
<th>Exploration Company</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Madagascar</td>
<td>Green Giant</td>
<td>Tolagnaro-Ampalaly Complex, Graphite Beds</td>
<td>800-580</td>
<td>Ore up to over 10 % TOC (mined)</td>
<td>60 Mt V₂O₅ (cut-off 0.5 %)</td>
<td>Nextsource Materials Inc.</td>
<td>Scherba et al. 2018</td>
</tr>
<tr>
<td>Mozambique</td>
<td>Balaam</td>
<td>Xixano Complex</td>
<td>800-600</td>
<td>Ore up to 17.5 % TOC (mined)</td>
<td>1.422 Mt at 0.2 % V₂O₅</td>
<td>Syrah Resources</td>
<td>Dickinson 2015</td>
</tr>
<tr>
<td>Mozambique</td>
<td>Nicanda Hill</td>
<td>Xixano Complex</td>
<td>800-600</td>
<td>Ore mean 10.7 % TOC (mined)</td>
<td>3.93 Mt V₂O₅</td>
<td>Triton Minerals</td>
<td>Dickinson 2014</td>
</tr>
<tr>
<td>Mozambique</td>
<td>Cualia</td>
<td>Xixano Complex</td>
<td>800-600</td>
<td>Up to 29 % TOC (mined)</td>
<td>82 Mt V₂O₅</td>
<td>New Energy Minerals</td>
<td>New Energy Minerals 2019</td>
</tr>
<tr>
<td>East Antarctica</td>
<td>Tanzania-Kenya</td>
<td>Tuavorite gems deposits</td>
<td>720-630</td>
<td>25-30 vol% graphite</td>
<td>Rich in vanadian micas</td>
<td>(not commercial)</td>
<td>Schlüter et al. 2011</td>
</tr>
<tr>
<td>Korea</td>
<td>Daejon</td>
<td>Changri Fm.</td>
<td>600-500</td>
<td>Up to 57 % TOC (mined as coal)</td>
<td>248 Mlbs</td>
<td>Optiro</td>
<td>Jeong 2006</td>
</tr>
<tr>
<td>China</td>
<td>Baiguoyuan</td>
<td>Doushantuo Fm.</td>
<td>600-540</td>
<td>Up to 4.9 % TOC (shale gas potential)</td>
<td>1 Bt ore in Chinese</td>
<td>Huili Resources</td>
<td>Zhuang et al. 1998</td>
</tr>
<tr>
<td>Czech Republic</td>
<td>Alabama, USA</td>
<td>Blivoe Complex</td>
<td>560-535</td>
<td>Up to 4.9 % TOC</td>
<td>2.01 Mt ore</td>
<td>(not commercial)</td>
<td>Kursweil et al. 2015</td>
</tr>
<tr>
<td>Oman</td>
<td>Coosa</td>
<td>Ediacaran-Cambrian Higgins Ferry Gp. Ediacaran-Cambrian boundary</td>
<td>540</td>
<td>Graphite (mined)</td>
<td>Up to 4000 ppm V₂O₅</td>
<td>Westwater Resources</td>
<td>Dean 2002</td>
</tr>
<tr>
<td>Kazakhstan</td>
<td>Karatau</td>
<td>Lower Cambrian</td>
<td>530</td>
<td>8-10 % TOC (resource)</td>
<td>2.01 Mt ore</td>
<td>(not commercial)</td>
<td>Balusa</td>
</tr>
<tr>
<td>China</td>
<td>Yangjiabe and others</td>
<td>Lower Cambrian 'stone coal'</td>
<td>15 to 25 % TOC on average</td>
<td>118 Mt V₂O₅ (Zhang et al. 2011)</td>
<td>Rentian Mining Ltd.</td>
<td>Zhong et al. 2011,Dai et al. 2018</td>
<td></td>
</tr>
</tbody>
</table>

TOC: Total Organic Carbon.

3. Vanadium in carbon-rich sediments in the Cryogenian-Cambrian

Carbon-rich sediments were deposited following the late Neo-proterozoic 'Snowball Earth' glaciations, when the oceans were flooded with fresh nutrients which supported extensive microbial growth (Plana
vsky et al. 2010). The development of anoxia, promoting the preser-
vation of organic carbon, continued through the Cambrian, most notably in the Upper Cambrian Alum Shale in Europe. This period of about 200
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Fig. 2. Increase in V abundance in Neoproterozoic, recorded by (i) maximum V content in black shales (Sahoo et al. 2012), (ii) V content in marine pyrite, expressed as ratio to long-term mean content (Mukherjee & Large 2020), and (iii) number of V minerals (Moore et al. 2020).
content scales with the carbon content. This means that a typical back association of exceptional carbon and exceptional V implies that the V content that is moderately rich but not commercially viable. For instance, V-rich sediments that are not richer in pyritic shales may have a V range of actual and potential V deposits (Table 1), and also anomalously not richer in pyritic shales.

up to 1.85 % TOC, have a mean 233 ppm V (Sperling et al. 2016). Unlike shale with a few % TOC, rather than an exceptionally rich black shale able as an alternative carbonaceous product such as oil or shale gas. The Cryogenian-Cambrian record of the vanadium-carbon association includes three particular stages that are distributed over a large area. The oldest is the Neoproterozoic Mozambique Belt in East Africa (broadly dated at 800–600 Ma), particularly in Madagascar and Mozambique. There are Lower Cambrian deposits across much of southern China, and possibly related deposits in adjacent Korea, Kazakhstan and the Baikal region of Siberia. In Europe, deposits are dominated by the Upper Cambrian Alum Shale, and the immediately following (Tremadoc = basal Ordovician) Dictyonema Shale, in Sweden and the Baltic States.

4. Discussion

4.1. Transfer of vanadium from volcanic rocks

The data show that Neoproterozoic igneous provinces provided a high mass of vanadium to the surface, and that on the Neoproterozoic sea floor anoxic sediments incorporated a high mass of vanadium. In addition to the systematic processes of weathering, erosion and transport that link the two together, the mid-Neoproterozoic witnessed the exceptional imprint of at least two global glaciations, the first of which lasted for tens of millions of years. The huge scale at which Neoproterozoic glacial erosion transferred mass from continent to ocean is evident from a local thickness of glacial debris exceeding 3 km (Young & Gostin 1989), denudation of at least 6 km in North America over 850–680 Ma deduced by thermochronology (DeLucia et al. 2018) and an estimated global erosion through 3–5 km due to glaciation (Keller et al. 2019). The Neoproterozoic glacial erosion has been invoked to explain the delivery of anomalous quantities of phosphorus (Horton 2015), copper (Parnell & Boyce 2019), and nutrients in general (Planavsky et al. 2010) to the oceans, and the evidence indicates that anomalous V was similarly delivered.

4.2. Stratigraphic record of vanadium deposits

The abundance of V deposits in Cryogenian-Cambrian carbon-rich rocks reflects the peak in black shale sedimentation identified by Condie et al. (2001). Within that interval, rocks deposited under anoxic conditions are represented particularly by the Neoproterozoic Mozambique Belt in East Africa, Lower Cambrian deposits across much of China, and the Upper Cambrian Alum Shale and equivalents in northern Europe. The distribution of V deposits maps onto this distribution of anoxic sediments. Notably, these three sub-episodes are in different parts of the globe (and were also during the Cambrian), implying that the source of V was in globally distributed ocean water rather than a discrete source.

4.3. Consequences for vanadium exploration

The biggest peak in black shale sedimentation in Earth’s history was in the Palaeoproterozoic (~2.0 Ga). However, although there are many other types of ore deposits related to these rocks (Parnell et al. 2021), there is little recorded concentration of vanadium. This implies that the abundance of carbon was not the sole factor behind V accumulation. The data from igneous provinces shows that there was a readily available source of V in the Neoproterozoic, which was newly mobile as the atmosphere became oxygenated. Exploration in carbon-rich sediment is therefore best focussed on the Neoproterozoic and younger successions.

Future exploration is most likely to be successful in extensions to the three large belts in the Neoproterozoic of East Africa, Lower Cambrian of China, and the Upper Cambrian in northern Europe. In East Africa, there are discoveries of graphite in Ethiopia, Sudan and Egypt in the northern equivalent of the Mozambique Belt, where exploration for trace elements including vanadium could be undertaken (Asia Pacific Gold Mining Investment Ltd. 2013). The Lower Cambrian deposits in China are widespread, and exploration benefits from historical artisanal mining of stone coal as a domestic fuel. A range of technologies are being assessed to release the vanadium from the stone coal matrix (Peng 2019,
Wang et al. 2020). The extraction of vanadium from stone coal would be done in combination with the extraction of other elements including rare earth elements and platinum group elements (Dai et al. 2018, Wu et al. 2021). The Lower Cambrian Karatau deposit in Kazakhstan could similarly be co-exploited for other metals (Kenzhaliyev et al. 2021). Vanadium exploration in the Upper Cambrian in Europe is currently problematic because of environmental considerations, although several potential sites in Sweden have been identified (Tellerreport 2019). However, this potential may yet be realised, as geopolitical considerations become more urgent. Not only is much of the world’s vanadium produced in China, but many deposits in other countries are financed by, and destined for, China (Barrera 2020).

Where both resources are co-located (Fig. 6), the co-exploration of vanadium and carbon (graphite) has obvious advantages in terms of shared infrastructure and other costs. This is especially relevant in East Africa where companies can licence for both vanadium and graphite (Syrah Resources Ltd. 2021). The association is regarded as fortuitous, but the evidence of this review is that it is not. As both commodities are required for future batteries, they can be cast as jointly contributing to the needs of green energy technology. While vanadium in East Africa is associated with resources of graphite, the Cambrian deposits in China are associated with less ordered carbon, which is used as a fuel in power stations and the domestic market (Dai et al. 2018).

### Table 2
Vanadium contents in volcanic rocks in Neoproterozoic igneous provinces.

<table>
<thead>
<tr>
<th>Igneous Province</th>
<th>Locality</th>
<th>Stratigraphy</th>
<th>Number analyses</th>
<th>Mean V (ppm)</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>Franklin</td>
<td>Alaska</td>
<td>Kilikktat Volcanics</td>
<td>21</td>
<td>330</td>
<td>Cox et al. 2015</td>
</tr>
<tr>
<td>Franklin</td>
<td>Coppermine</td>
<td>Coronation sills</td>
<td>20</td>
<td>343</td>
<td>Bédard et al. 2016</td>
</tr>
<tr>
<td>Franklin</td>
<td>Victoria Island</td>
<td>Natzuak Basalt</td>
<td>24</td>
<td>343</td>
<td>Williamson et al. 2016</td>
</tr>
<tr>
<td>Franklin</td>
<td>Corporation Gulf</td>
<td>Coronation sills</td>
<td>19</td>
<td>387</td>
<td>Shelnutt et al. 2004</td>
</tr>
<tr>
<td>Franklin</td>
<td>Murray Island</td>
<td>Coronation sills</td>
<td>10</td>
<td>400</td>
<td>Bédard et al. 2016</td>
</tr>
<tr>
<td>Franklin</td>
<td>Somerset, POW islands</td>
<td>Dikes</td>
<td>7</td>
<td>356</td>
<td>Bédard et al. 2016</td>
</tr>
<tr>
<td>Franklin</td>
<td>NW Greenland</td>
<td>Franklin-Thule sills</td>
<td>4</td>
<td>377</td>
<td>Kettanah et al. 2016</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Weighted mean</td>
<td>167</td>
<td>351</td>
<td></td>
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<tr>
<td>Gairdner</td>
<td>Stuart Shelf</td>
<td>Bitter Springs Volcanics</td>
<td>3</td>
<td>337</td>
<td>Zhao et al. 1994</td>
</tr>
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<td>Gairdner</td>
<td>Adelaide Fold Belt</td>
<td>Wooltana Volcanics</td>
<td>7</td>
<td>351</td>
<td>Foden et al. 2002</td>
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<tr>
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<td>Wooltana Volcanics</td>
<td>14</td>
<td>320</td>
<td>Wang et al. 2010</td>
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<td>Beda Basalt</td>
<td>9</td>
<td>357</td>
<td>Wade et al. 2014</td>
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<tr>
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<td>Amata Suite</td>
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<td>Zhao et al. 1994</td>
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<td>Wang et al. 2010</td>
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<td>18</td>
<td>346</td>
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<td></td>
<td></td>
<td>Weighted mean</td>
<td>61</td>
<td>346</td>
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<td>Anti-Atlas Supergroup</td>
<td>Morocco</td>
<td>Ait Ahmane-Khazma Ophiolite</td>
<td>10</td>
<td>310</td>
<td>Hoel et al. 2020</td>
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<td>Fettes et al. 2011</td>
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<td>Farragon Beds</td>
<td>12</td>
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<td>Goodman &amp; Winchester 1993</td>
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<tr>
<td></td>
<td></td>
<td>Weighted mean</td>
<td>43</td>
<td>376</td>
<td></td>
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<td>Vołyn-Brest</td>
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<td>Biłotowska et al. 2002</td>
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<td>Volyn Series</td>
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<td>361</td>
<td>Nosova et al. 2008</td>
</tr>
<tr>
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<td>Moldova-Belarus-Ukraine</td>
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<td>16</td>
<td>397</td>
<td>Študor et al. 2019</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Weighted mean</td>
<td>45</td>
<td>369</td>
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</tr>
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**Fig. 4.** Global palaeogeography at 630 Ma (after Li et al. 2008), showing location of Neoproterozoic igneous provinces (Gairdner, Franklin, Anti-Atlas, Vołyn) with V-rich basalts.

**Fig. 5.** Graphitic schist containing V-rich micas, Neoproterozoic, Dronning Maud Land, East Antarctica (image courtesy of Jochen Schlüter, Cornelia Spiegel and colleagues, Hamburg and Bremen).
Fig. 6. Licence map for exploration for graphite and vanadium, Green Giant property, Madagascar. Licenced ground is contiguous, allowing efficient co-exploration.

5. Conclusions

Vanadium deposits related to carbon-rich sediments were formed particularly during Cryogenian-Cambrian time. The association reflects the availability of large amounts of vanadium in igneous provinces, the transfer of the vanadium into the oceans enhanced by global glacial erosion, and the deposition of anomalously carbon-rich sediments in which the vanadium accumulated.

The association is yielding vanadium in several parts of the world, and several more are at the exploration/development stage. There is good knowledge of where the carbonaceous host rocks are, including graphite deposits, which should focus the exploration for vanadium.

With better understanding of how the association was developed in Cryogenian-Cambrian time, further vanadium resources can be expected.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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