Vanadium for Green Energy: Increasing Demand but With Health Implications in Volcanic Terrains

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Abstract The transition to a clean energy future may require a very substantial increase in resources of vanadium. This trend brings into focus the potential health issues related to vanadium in the environment. Most vanadium enters the Earth's crust through volcanic rocks; hence, vanadium levels in groundwaters in volcanic aquifers are higher than in other aquifers and can exceed local guidance limits. The biggest accumulation of volcanogenic sediment on the planet is downwind of the Andes and makes up much of Argentina. Consequently, groundwaters in Argentina have the highest vanadium contents and constitute a global vanadium anomaly. The high vanadium contents have given rise to health concerns. Vanadium could be extracted during remediation of domestic and other groundwater, and although the resultant resource is limited, it would be gained using low-energy technology.

Plain Language Summary The green energy revolution will greatly increase the demand for vanadium resources, especially for vanadium-flow batteries. Most vanadium is a by-product of processing volcanic rocks for other metals. The affinity of vanadium for volcanic rocks is reflected in high vanadium contents in groundwaters in volcanic terrains, in some cases exceeding guidance limits for drinking water. A review of groundwater compositions across Argentina shows values greatly exceeding guidance limits due to a very large eastward flux of vanadium from mineralized volcanic rocks in the Andes. The vanadium could be extracted from groundwaters by developing low-energy technology.

1. Introduction

The high demand for vanadium in support of the green energy revolution will require a substantial increase in mining for new resources, possibly a 200% rise in annual demand by 2050 (World Bank, 2020). Vanadium is needed for vanadium-flow batteries, potentially on a very large scale (Colthorpe, 2021; Gencoten & Sahin, 2020; Zhang et al., 2019), in addition to the established demands for high-strength steel and electronics. However, there is an increasing awareness of the possible health hazards of high levels of vanadium in the environment (Amuah et al., 2021; Mitchell et al., 2011; Vasseghian et al., 2021; Ścibior et al., 2021). Excessive amounts of vanadium in the human body can affect the digestive system, the urinary tract, and the reproductive system and for example, cause anemia, kidney disease, asthma, dermatitis, and rhinitis (Jayawardana et al., 2015; Wilk et al., 2017; Yang et al., 2017). Exposure to vanadium in groundwater has also been implicated in birth defects (Hu et al., 2017). Health problems due to vanadium in groundwater may be exacerbated by co-occurrence with other toxic elements (Chen et al., 2022; Coyte & Vengosh, 2020). The concerns will rise as more vanadium mining takes place. The bulk of vanadium is obtained from ores in volcanic rocks containing the mineral titanomagnetite, in which vanadium is a trace element (Gilligan & Nikoloski, 2020; Yang et al., 2021). There are specific concerns about the consequences for human health of mining and processing titanomagnetite ores for vanadium (Makhotkina & Shubina, 2014; Yu & Yang, 2019; Zhang et al., 2020). There is an appreciation that volcanic activity in general introduces trace elements, including vanadium, that can be toxic to humans (Duntas, 2016; Nahar, 2017).

The aims of this study are to:

1. Review data about V contents of groundwater in volcanic rocks in comparison with other nonvolcanic groundwaters and legislative limits for drinking water.
2. Assess where the occurrence of V-rich groundwaters in volcanic rocks might be most acute.
3. Make a preliminary assessment of whether the cleanup of high V contents in groundwaters could be linked to the extraction of V as a resource.
2. Groundwater in Volcanic Rocks

The high input of volcanic matter is potentially an environmental problem for Argentina. In other parts of the world, where groundwater occurs in volcanic rocks, the water contains anomalously high amounts of vanadium (Table 1; Figure 1). The water becomes enriched in vanadium by dissolution of the volcanic minerals and glass. The benchmarks against which to assess water compositions vary between countries (Table 2) but values include a health reference limit of 21 μg/L in tap water by the U.S. Environmental Protection Agency (Environmental Working Group, 2021) and lower limits for groundwater in some European countries (Länderarbeitsgemeinschaft Wasser, 2004; Smit, 2012). There is no statutory limit for the whole European Union, where vanadium values in some Italian groundwaters would probably exceed any limit due to volcanic activity (Crebelli & Leopardi, 2012). In Britain and Europe, mean groundwater vana-

Table 1
Mean Groundwater Contents of Vanadium in Aquifers in Volcanic Rocks and Detailed Data for Groundwater in Argentina and Adjacent Regions

| Country/Province | Volcanics | Data source | V (μg/L) | Data points | Reference |
|------------------|-----------|-------------|---------|-------------|-----------|
| Italy, Central   | Plio-Pleistocene | Water in volcanics | 13      | 214         | Cinti et al., 2015 |
| Italy, Central   | Plio-Pleistocene | Water in volcanics | 36      | 7           | Sappa et al., 2014 |
| Italy, Mt. Etna  | Recent    | Water in volcanics | 57      | 10          | Marczewski et al., 2015 |
| Italy, Mt. Vulture | Pleistocene | Water in basalt, pyroclastics | 36      | 34          | Parisi et al., 2011 |
| Serbia           | Paleogene | Water in andesites | 7.9     | 2           | Petrovic Pantić et al., 2015 |
| Iran             | Quaternary | Water in andesites | 32      | 16          | Ghoreyshinia et al., 2020 |
| Ethiopia         | Quaternary | Hot springs in volcanics | 10      | 12          | Rango et al., 2010 |
| Djibouti         | Quaternary | Water in basalt | 65      | 13          | Ahmed et al., 2017 |
| Tanzania         | Recent    | Water in volcanics | 18      | 48          | Tomašek et al., 2022 |
| Canary Islands, El Hierro | Quaternary-Recent | Water in basalt | 101     | 173         | Luengo-Oroz et al., 2014 |
| Madeira, Porto Santo | Miocene   | Water in basalt and hyaloclastites | 109    | 16          | Condeço de Melo et al., 2020 |
| Iceland          | Recent    | Water in volcanics | 5       | 166         | Barbieri et al., 2021 |
| Iceland, Hekla   | Recent    | Water in volcanics | 16      | 4           | Holm et al., 2010 |
| Korea, Jeju      | Quaternary | Water in volcanics | 13      | 53          | Koh et al., 2016 |
| Japan, Mt. Fuji  | Pleistocene-Recent | Water in volcanics | 64      | 5           | Kato et al., 2004 |
| Kamchatka, Russian Far East | Recent | Water in thermal springs | 219    | 6           | Bortnikova et al., 2009 |
| Hawaii           | Holocene  | Water in lava tubes | 74      | 5           | Prouty et al., 2017 |
| Hawaii           | Holocene  | Groundwater | 40      | 12          | McCleskey et al., 2020 |
| USA, northwestern | Miocene (Columbia River) | Water in basalt | ~10     | >20         | Newcomb, 1972 |
| Scotland, UK     | Devonian, Carb., and Paleogene | Water in volcanics | 2.2     | 29          | MacDonald et al., 2017 |
| Germany, Eifel   | Pleistocene | Water in volcanics | 17      | 7           | Härtter et al., 2020 |
| Germany, Saar-Nahe Basin | Permo-Carboniferous | Water in mixed volcanics and sediment | 19–48   | range       | Leiviská, 2021 |
| Argentina (Tucumán) | Shallow wells Aquifers | 31–300 (median 77) | 42      | Nicoli et al., 2012 |
| Argentina (Salta) | Aquifer spring | 1–15 (median 4 and mean 6) | 10      | Concha et al., 2010 |
| Argentina (Córdoba) | Aquifers Aquifers | 10–670 (median 30 and mean 66) | 66      | Farías et al., 2003 |
| Argentina (Santiago del Estero) | Aquifers | 30–2,710 (mean 995) | 9     | Pérez-Carrera & Curelli, 2013 |
|                  |           |              |         | 6–1,003 (median 35 and mean 132) | Bhattacharya et al., 2006 |
Table 1  
Continued

| Country/Province          | Volcanics   | Data source | V (μg/L)                  | Data points | Reference                        |
|---------------------------|-------------|-------------|---------------------------|-------------|-----------------------------------|
| Argentina (Santa Fe)      | Aquifers    |             | 76–1,090 (median 160 and  | 15          | Siegfried et al., 2015            |
|                           |             |             | mean 249)                 |             |                                   |
| Argentina (Chubut)        | Aquifers    |             | 100–2,500 (median 800 and mean 918) | 14          | Del Pilar Alvarez & Carol, 2019   |
| Argentina (Buenos Aires)  | Aquifers    |             | 50–2,470 (median 510 and mean 548) | 101         | Fiorentino et al., 2007           |
|                           |             |             | 13–1,380 (mean 430)       |             | Bonorino et al., 2008             |
|                           |             |             | 40–800                    |             | Espósito et al., 2011             |
|                           |             |             | 141–556 (median 325 and mean 330) |             | Puntoriero et al., 2014           |
| Argentina (Neuquen)       | Aquifers    |             | 106–1,184 (median 146 and mean 266) | 8           | Farnfield et al., 2012            |
| Argentina (San Luis)      | Aquifers    |             | 27–164 (median 72)        | 11          | Galindo et al., 2007              |
| Argentina (Rio Negro)     | Aquifers    |             | 1–113 (median 64 and mean 30) | 20          | Al Rawahi & Ward, 2017            |
| Argentina (La Pampa)      | Aquifers    |             | 20–5,400 (median 560 and mean 840) | 108         | Smedley et al., 2002              |
|                           |             |             | 211–4,889 (median 1,486 and mean 1,620) | 30          | Al Rawahi & Ward, 2017            |
|                           |             |             | 1,156–2,472 (mean 1,749) | 3           | Jaafar et al., 2018               |
|                           |             |             | 20–1,972 (mean 351)      | 32          | Alcaine et al., 2020              |
| Argentina (Chaco)         | Aquifers    |             | bdl–2,646 (median 76 and mean 204) | 45          | Giménez et al., 2013              |
| Bolivia                   | Aquifers    |             | 1–40 (median 8 and mean 11) |             | Muñoz et al., 2013                |
| Uruguay                   | Aquifers, potable |       | 3–167 (median 23 and mean 40) |             | Machado et al., 2020              |
| Paraná, S. Brazil         | Aquifers    |             | 5–135 (mean 22)          |             | Rezende et al., 2019              |

Dium contents are less than 1 μg/L (MacDonald et al., 2017; Shand et al., 2007; Smit, 2012). A content of >15 μg/L vanadium in drinking water has been suggested as a potential health risk in the State of California, USA (Gerke et al., 2010).

The collated data for mean groundwater compositions in volcanic aquifers from several parts of the world show that:

1. The vanadium values are consistently higher than in nonvolcanic aquifers as represented by the British and European values.
2. In several cases, the vanadium values exceed the statutory limits set by some countries.
3. Aquifers in old volcanic rocks from the pre-Pleistocene geological record also show values higher than nonvolcanic aquifers.

In several of these regions, there is concern about the importance of groundwater vanadium for human health, including Italy (Arena et al., 2015), Germany (Härter et al., 2020), and the Canary Islands (Luengo-Oroz et al., 2014).
3. Andean Mineralization and Groundwater in Argentina

Given the implication of greater V contents and thus greater potential implications for health, in groundwaters in volcanic rocks, we can predict where this issue might be most acute. The extent of volcanic rocks, or sediments derived from volcanic rocks, is imposed by plate tectonics and patterns of plates on Earth over the last 100 million years. The requirements for very extensive volcanic-related aquifers are (a) long-term plate boundary subduction, causing long-term volcanic activity; (b) long length of boundary, as opposed to the short arcs that typify the west Pacific Rim; and (c) continued uplift to promote erosion of volcanics and their deposition as a sediment wedge, built up above sea level. These requirements are met most clearly in South America, where the Andes
represent over 8,000 km subduction trench length, persistent volcanic activity, and uplift (Sundell et al., 2019) that have sourced sediment to the east. The Andes have been a plate margin mountain chain for tens of millions of years (Evenstar et al., 2015) and have shed enormous volumes of sediment eastward across Argentina. Importantly, Westerly winds have supplemented the eroded volcanic sediments with volcanic glass and ash (Mingari et al., 2017). Petrographic studies confirm that the sediment in Argentina and Chile contains volcanic debris derived from the Andes by mechanical erosion (Gómez et al., 2020; Horton, 2018) and volcanic glass. Magnetite grains in the sediment, in which much vanadium may be exported from the Andes, show evidence of alteration (Flint et al., 1986), which would have released the vanadium into groundwaters.

Reserves of vanadium-bearing titanomagnetite are greatest in South Africa, Russia, and China (Summerfield, 2019; Yang et al., 2021). In addition, large amounts of titanomagnetite in the Chilean Andes are mined for iron ore and contain high levels of vanadium (Broughm et al., 2017; La Cruz et al., 2020; Palma et al., 2020). Mining of iron and copper in the Andes has caused its own health concerns (Carkovic et al., 2016; Cortés et al., 2021; Reyes et al., 2020; Tapia et al., 2018). In addition to the release of toxic metals from mining spoil, the same mineralized volcanic rocks have been releasing trace elements into the environment through natural erosion over a geological timescale. The mountains are composed of magmatic rocks, which are mineralized by a range of ores including vanadium-bearing titanomagnetite. The titanomagnetite grains exhibit alteration and dispersion of the vanadium (Figure 2). Mineral alteration in the volcanic rocks and subsequently during erosion and transport could release most or all of the vanadium into groundwaters that composes Argentina.

The influence of volcanic matter on groundwater is on a larger scale in Argentina than elsewhere. There is some local concern over vanadium contents in domestic groundwater in Argentina (Espósito et al., 2011; Jaafar et al., 2018; Nicolli et al., 2012), but this has been overshadowed by concern about arsenic contamination over much of South America (Bundschuh et al., 2021; Khan et al., 2020). However, here, we bring together diverse data sets, which show that high vanadium levels occur in groundwater across Argentina and represent the largest known region of concern for vanadium toxicity.

Twenty data sets for groundwater (Table 1) represent 12 provinces along the length of Argentina (Figure 3). The mean values for V range from 6 to 1,749 μg/L. The highest individual value is 5,400 μg V/L, recorded in La Pampa Province (Smedley et al., 2002). The lowest mean value is in Salta Province in the far north near the Bolivian border (Figure 3). There is a broad distinction between values in the northern provinces (Tucumán, Salta, Córdoba, Santiago del Estero, Chaco, Santa Fe, and San Luis) and those in the south (Buenos Aires, La Pampa, Neuquén, Rio Negro, and Chubut). The weighted mean for the northern provinces is 150 μg V/L (n = 235). The weighted mean for the southern provinces is 696 μg V/L (n = 338), nearly 5 times as high. The southern provinces lie east of the major volcanoes in the Andes (Figure 3) and they would have a greater fingerprint of their output.

| Region                          | Baseline values | V Content (μg/L) | Reference                          |
|---------------------------------|-----------------|-----------------|------------------------------------|
| England/Wales                   | Groundwaters    | Median <1       | Shand et al., 2007                 |
| Scotland                        | Groundwaters    | Median 0.4      | MacDonald et al., 2017             |
| Sweden                          | Bottled water   | Median 0.39     | Rosborg et al., 2005               |
| Europe                          | Filtered water  | Median 0.46     | Smitt, 2012                        |
| USA (Environmental Protection Agency) | Health reference concentration | Median 21       | Environmental Working Group, 2021  |
| USA                             | Benchmark values| 20 chronic (long-term exposure) | Suter & Tsao, 1996                 |
|                                 |                 | 280 acute (short-term exposure) |                                     |
| USA                             | Potential health risk | Median 15       | Gerke et al., 2010                 |
| Netherlands                     | Legal limit     | Median 3        | Smit, 2012                         |
| Germany                         | Guide limit     | Median 4        | Länderarbeitsgemeinschaft Wasser, 2004 |
| Croatia                         | Drinking water limit | Median 5       | Demetriades et al., 2012           |
| Serbia                          | Drinking water limit | Median 1       | Demetriades et al., 2012           |
| China                           | Legal limit     | Median 50       | Li et al., 2020                     |
The immediately surrounding countries of Bolivia, Uruguay, and southern Brazil also yield mildly anomalous groundwater data with mean values of 11, 40, and 22 μg V/L, respectively (Machado et al., 2020; Muñoz et al., 2013; Rezende et al., 2019). However, these mean values for vanadium in groundwater are lower than most of the mean values reported in Argentina and suggest a progressive decline with distance from the source of vanadium.

4. Mitigation

There are strategies available to mitigate high vanadium contents in groundwaters, intended primarily to cope with contamination from mining and other short-term commercial activities. The methods include adsorption onto iron oxides, activated carbon, liquid membranes, and combinations of these materials (e.g., Kamal et al., 2017; Leiviskä, 2021; Sirviö et al., 2016; Sharififard et al., 2016). The emphasis has been in the removal of a toxic element, but there is a move toward sustainability using innovative extraction of V from wastewater and V-rich solutions (Petranikova et al., 2020).

Figure 2. Element maps (Fe, Si, Ca, and V) for magnetite grains in andesite, Quebrada Cerrillos, Copiapo, Chile. Maps for Fe and Si show alteration, especially along fractures, and growth of Si-rich alteration phases. Map for Ca also shows mineral alteration along fractures and additionally beyond periphery of grain. Map for V shows spread of V beyond periphery into the altered area.
The mean V content of sea water is much lower than in the groundwaters discussed, commonly cited as 0.3 μg/L and up to ∼2 μg/L. The extraction of vanadium from seawater is possible (Ivanov et al., 2017; Suzuki et al., 2000) but not economically feasible. Extraction from groundwater would be more economic if the large scale was not essential. Groundwater with a V content of 100 μg V/L in 10% aquifer porosity would contain $10^4$ kg V. Given the

**Figure 3.** Map of southern South America, including provinces of Argentina, showing mean values for data sets of vanadium contents (μg/L) in groundwater. Data are listed in Table 1.
rate at which groundwaters move in Argentina, estimated as 0.01–0.42 m/day and more specifically in one study as 0.07 m/day (Cabrera et al., 2010, 2017; Maldonado et al., 2016), groundwaters with 100 μg V/L in 10% aquifer porosity would be replenished within 40 years. Less conservative values of 20% porosity and 200 μg V/L would see replenishment of all the groundwater V within 10 years. The quantities of V that could be obtained from groundwater sources may be limited but the technology has the advantage of low temperature and low energy processing. Incidentally, the mass of V in a large ore body of 10^8 kg vanadium in sandstone (Kelley et al., 2017) would be sourced in less than a million years in the 1 km^3 of groundwater.

Most of the data are from groundwaters in relatively young (<5 Ma) volcanic rocks. An example that includes older (>100 Ma) volcanic rocks, in Scotland, includes groundwaters with several times the V contents for the region (MacDonald et al., 2017). However, the contents are modest compared with the values in young volcanic rocks. This implies that volcanic rocks release much of their mobile V when they are young, probably from reactive volcanic glass and unstable magmatic minerals. A further implication is that if large volumes of volcanogenic sediment can be identified in the geological record, they could have hosted V-rich groundwaters and even sediment-hosted V mineralization.

5. Conclusions

This review of V contents in groundwaters in volcanic terranes confirms previous implications that they are higher than in nonvolcanic terranes. In particular.

1. In several aquifers in volcanic rocks, the mean vanadium values exceed the statutory limits of some countries.
2. The anomalously large volume of volcanogenic sediment contributed from the long-term erosion of the Andes is reflected in the very high groundwater V levels in Argentina.
3. The high V contents in groundwaters in young volcanic rocks suggest that the V is liberated early in the rock history.

Faced with a possibly very big increase in the demand for vanadium to support battery manufacture, new and more environmentally acceptable technologies, and new sources of vanadium, may be required. A new landscape for the processing of vanadium must take into account the potential implications for human health. The data suggest that V-rich groundwaters may incidentally make a modest contribution to resources of the element.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

All data are reviewed from published literature and included in this paper.

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