GEOBROWSER

Culprit for a major global cooling event is identified

For many years scientists have been aware that a dramatic climatic cooling event occurring in 1831 must have been caused by a volcanic eruption, but in a classic case of a 'known unknown' its location was a mystery. This has now been solved, according to a National Academy of Science publication in December 2024. Using Polar ice cores showing volcanic ash layers deposited at various times over the past 2500 years, a team from the University of St Andrews were able to prove that the andesitic to dacitic composition of the ash layer deposited in 1831 (as cryotephra) exactly matches that of tephra analysed from the andesitic Zavaritskii volcano on the now-uninhabited Simushir island, part of the Kuril-Kamchatka volcanic arc system lying to the north of Japan (*doi.org/10.1073/pnas.2416699122*). This was evidently a Pelean-type eruption, and such was its explosive force that it left behind an impressive caldera, with a rim-to-rim diameter of ~6 km. Historical records provided additional confirmation of the time of eruption; for example on a nearby island the youngest mappable Zavaritskii tephra layer overlies a rusted gun as well as a hoard of muscovite imported for windowpanes, both typical of the Russian colonial period which spanned the 1700s to early 1800s.

The research team scored the Zavaritskii eruption at magnitude 5–6 on the Volcanic Explosivity Index (VEI), similar to that for the 1991 Pinatubo eruption in the Philippines, but not on the scale of a supervolcano, which would require a magnitude of 8 or over (the 1815 Tambora eruption comes close, with a VEI of 7). Its global cooling effect was attributed to the stratospheric injection of tonnes of sulphur dioxide and other particulates, almost twice as much as that calculated for the 1991 Pinatubo eruption and well capable, it is thought, of causing climatic effects such as the droughts recorded between 1831 and 1838 in Africa and India. In Europe its effects are reflected in the diary entry by the composer Felix Mendelssohn, while on holiday in the Alps during the summer of 1831. He noted: '*Desolate weather, it has rained again all night and all morning, it is as cold as in winter, there is already deep snow on the nearest hills…*' The cooling may have been immediate, since a paper in Geology Magazine for 2018 (*https://doi.org/10.1130/G45092.1*) suggests that eruptions of this type can cause sudden and widespread climatic changes due to the process of electrostatic levitation, which injects volcanic particles directly into the ionosphere ensuring their rapid global distribution.

The Zavaritskii caldera on Simushir Island

The flooded Broutona Bay caldera, with buildings of the now-derelict submarine base shown in the foreground. The base lies at the foot of an extinct or possibly only dormant pre-caldera volcano, which probably represents a later resurgence of activity within the Broutona caldera (Photographs kindly supplied by Tony Waltham)

All of this suggests that the Kuril volcanic chain may provide fertile ground for geochemically 'fingerprinting' other Arctic ash layers. Further sources may be found farther north along the Kamchatka Peninsula, where there is a chain of similar andesitic volcanoes with long repose periods. They include Shiveluch volcano, which has been erupting since explosive activity was renewed in 1854, and Bezimianney, which was actually considered extinct until explosive eruptions commenced in 1955, culminating in a massive lateral-blast eruption. In late July this year a major eruption of the Klyuchevskoy volcano, only a few hours after a massive 8.8 magnitude earthquake, was followed by five more eruptions from volcanoes in the same region: testifying to Kamchatka's continuing ativity.

In the north of Simushir Island the Broutona Bay caldera is similar in size to Zavaritskii but older and as yet undated. This caldera's flooded northern part, which probably reflects the result of a lateral blast, was chosen to host a secret Russian Cold War nuclear submarine base which also lies at the foot of a large, pre-caldera volcano. The base operated from 1987 but was dismantled during Putin's early presidency in 1994. Russia's economy was ailing at this time, and the on-going and ultimately abortive START II arms limitation negotiations would have provided a convenient excuse for the cut-back.

Another very large geode

Last year's Geobrowser highlighted a spectacular geode in the Almeria Province of Spain; but Tony Waltham has pointed out that there is another, much larger crystal-lined cavity in the Chihuahua Province of Mexico (Badino *et al. The Naica Caves Survey, 15th International Congress of Speleology, 2009)*. The 'Cave of the Crystals, or Giant Crystal Cave (Spanish: *Cueva de los cristales*) is inaccessible and was only

found by chance, in April 2000, during exploration drilling around a mineral deposit containing ores of lead, zinc and silver. By far the most spectacular of a number of other crystal-lined caves connected to these mine workings, it lies at a depth of 300 metres and measures 109 metres (358 ft) long with a volume of 5000 to 6000 cubic metres. Like the Almeria geode it is hosted in limestone, and the crystals of selenite, which is an isomorph of gypsum ($CaSO_4$ $2H_2O$), are among the largest natural crystals ever found. One measures 11.40 metres, with a volume of about 5 cubic metres and an estimated mass of 12 tonnes.

Uranium-thorium dating by Stein-Erik Lauritzen (University of Bergen, Norway) suggests that the crystals' maximum age is about 500 000 years, but the crystals continue to enlarge each time the cave is flooded. One research team has worked out a growth rate which is the slowest for any crystal growth process. Taking this into account, the largest crystals would have taken approximately one million years to reach their current size. It seems that a magma chamber approximately 3–5 km below the cave heated groundwater above it, which then became saturated with sulphide ions. Upon encountering cooler descending surface waters the sulphide ions were oxidised to sulphates, which then precipitated as anhydrite. This then dissolved when the cave temperature dropped below 56°C, which is when the gypsum crystals formed.

Unlike the Almeria geode, the cave is unlikely to ever become a tourist attraction. Firstly, it is commonly flooded, and even when dry the air temperatures reach up to 58°C, with 90 to 99 percent humidity, meaning that without proper protection, involving special suits that circulate ice-cooled water, a person can only endure approximately ten minutes of exposure at a time. The cave also needs to be frequently closed off to allow the crystals to grow further.

Minerals in the firing line

By the time this Journal goes to press, much will have been said, and perhaps decided, about how best Ukraine can utilise its mineral wealth, which will ultimately prove vital for stabilising its economy and maintaining its sovereignty if and when peace with Russia is established. The issue became mainstream news during the course of February this year, but as reported by Tom Watling (*Independent* for 25 February), Ukraine's President Zelensky had been trying for some years to develop these resources, which are estimated to be worth more than £12 trillion based on figures provided by Forbes Ukraine. In 2021, for example, he offered outside investors tax breaks and investment rights to help exploit these minerals, and in 2024 he placed minerals mining into the victory plan he drew up to thwart Russia's invasion. There has been much focus on rare earth resources, but the interest from American President Trump also included the acquisition of 'techno' elements such as graphite, titanium and lithium.

Ukraine has a complex and varied geological terrain, which includes a central basement belt of Archaean and Proterozoic rocks overlain by Palaeozoic, Mesozoic and Cainozoic sedimentary strata. A map provided by Ukrainian group *UnitedMedia 24* shows the location of critical mineral resources across the country, but this must be regarded with caution since some of the public domain information may date from Soviet-era surveys, and many prospects are not yet fully developed or even explored. There may be other occurrences which, for reasons of national security, remain secret. It is therefore not possible to attempt anything approaching a realistic inventory of Ukraine's riches, but here are just a few examples listed by *worldatlas.com*.

Cave of Giant Crystals, Naica (Courtesy of Geology In)

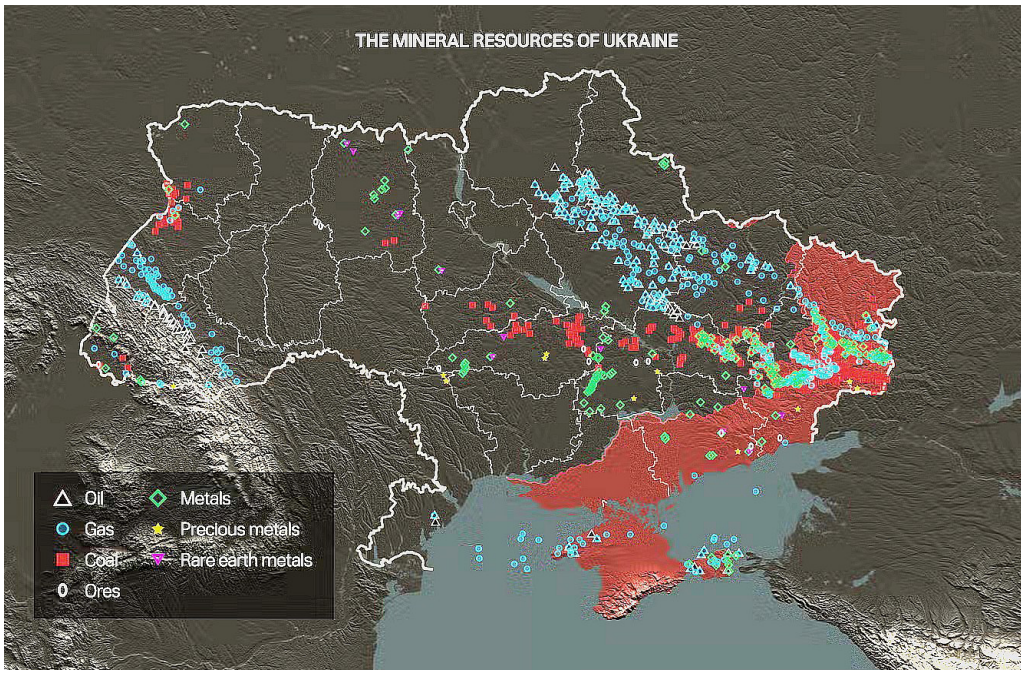
The country has deposits of 21 *rare earth elements* from the EU's list of 30 critical raw materials for the production of devices to develop 'green energy', particularly batteries. According to the Institute of Geology, Ukraine, these elements include: *lanthanum* and *cerium*, used in TVs and lighting; *neodymium*, used in wind turbines and EV batteries; and *erbium* and *yttrium*, whose applications range from nuclear power to lasers. EU-funded research also indicates that Ukraine has *scandium* reserves but detailed data is classified. Ukraine holds the largest *titanium* reserves in Europe and is currently producing 7% of the world's output. There are 15 known deposits with the four being explored situated in the Kharkiv, Kiev, Donetsk, and Dnipropetrovsk regions. *Lithium* reserves are largely untapped but considered to be one of Europe's largest at an estimated 500 000 tonnes. Ukraine's reserves of *graphite*, a key component in electric vehicle batteries and nuclear reactors, are located in the centre and west of the country and represent 20% of global resources (only China has more). Ukraine, Australia, and Russia have the biggest proportion of *iron ore* deposits in the world, each holding over 10% of the world's reserves. Ukraine alone has an estimated 27 billion tons and ranks sixth in global iron ore production. Ukraine is in the world's top ten producers of *manganese* ore and in 2010 it produced over 736 000 metric tons of marketable ores and concentrates, of which about one sixth were exported and the rest used domestically to produce ferroalloys. The country has the largest *uranium* deposit in Europe, accounting for 1.8% of the world's reserves.

Hydrocarbon resources constitute a further strategically important minerals sector to power a country which, given the present and likely future circumstances, will probably not be looking to de-carbonise its economy. *Coal* reserves are estimated to meet the demand for energy and industry in Ukraine for the next 500 years, accounting for 95% of the fossil fuel resource. The country has the world's 7th largest and Europe's 2nd largest coal reserve at about 34 billion tons: the high methane content does make this a risky resource to exploit, but offers the potential for shale gas extraction. *Natural Gas* reserves were estimated in 2004 to comprise over 1.1 trillion cubic metres, ranking it 26th among the countries with proven gas reserves before Crimea was annexed. *Gas condensate* reserves are in the region of 80 000 tons. Ukraine is also estimated to hold over 135 million tons of *oil* and 3.7 billion tons of *shale oil* reserves.

As this Journal goes to press there is one obvious problem: some £6 trillion of Ukraine's mineral resources, or about 53% of the country's total, are contained in the four front-line regions illegally occupied by Russia in September 2022. While a minerals extraction agreement between the USA and Ukraine was finally signed off and published on May 1st (*Website for the CSIS in Washington DC*), it is difficult to see how this could ever be enacted given Russia's continuing aggression and the lack of progress towards a lasting peace. Moreover, many experts have questioned the viability of minerals extraction in terms of time-frames, practicalities and cost-benefits. In particular, President Trump's focus on doing a 'deal' that would enable American companies to obtain Ukraine's rare earths may be misplaced according to some commentators (*e.g. IEEE Spectrum website for March 2025: 'Ukraine doesn't have mineable (rare earth) deposits'*).

...but there's always Greenland

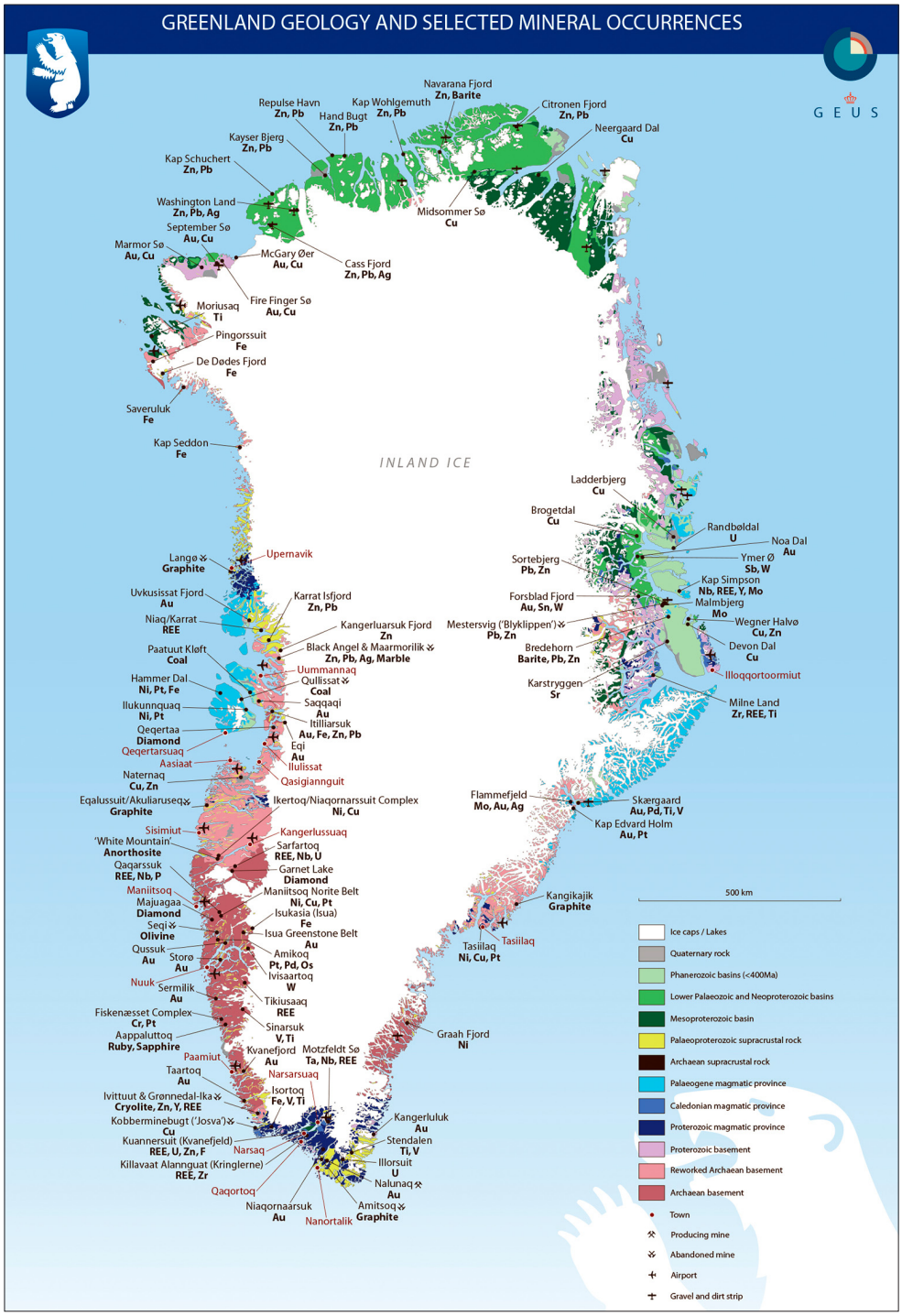
Should Trump's peace plan for the Ukraine-Russia conflict that also serves the interests of American companies fail to be delivered, there will be other parts of the world with sizeable onshore REE deposits (see



Principal mineral occurrences in Ukraine. The red areas show the extent of Russian incursion (Courtesy of UnitedMedia 24).

Colman and Waltham in *Mercian Geologist* for 2017, pp 102–106). Greenland, which is a self-governing territory of Denmark, is now in the firing line following Trump's pronouncement early this year that (one way or another) America will 'have to have it'. Whether this ambition stems from the USA's national strategic interests (already served by a long-standing defence treaty with Denmark) or simply a wish to add a '51st. State' and thus cement a place in history, Greenland's natural resources are bound to be a further motive. For example, one Greenland official has said that the island 'possesses 39 of the 50 minerals that the United States has classified as critical to national security and economic stability'.

Like Ukraine, Greenland's geology, summarised in the *Geology of Greenland Survey Bulletin* 185 (2000), is highly diverse, with Archaean and Proterozoic metamorphic basement overlain by Palaeozoic sedimentary rocks. There are also spectacular layered igneous complexes, related in age to the early Cainozoic Scottish Hebridean volcanic province. Past exploration programmes have shown that the ice-free fringes of the island contain a remarkable diversity of mineral prospects. These include rich deposits of nickel, copper, gold, platinum, cobalt, graphite, molybdenum, aluminium, lithium (the list goes on); there is also considerable potential for offshore oil and gas (*e.g. van Halm, Energy Monitor website for July, 2023*).



Map of Greenland mineral deposits (https://naalakkersuisut.gl/da/Naalakkersuisut/Nyheder/2017/12/0412_genforhandling).

The Greenland government administers 126 active exploration licences, with a further 46 being processed (as per April this year). There are however only two operating mines; the newly-opened Nalunaq underground gold mine, one of the richest in the world, and the White Mountain open-cast anorthosite mine. The Kvanefjeld mining project, owned by Greenland Minerals and Energy, is currently investigating one of the largest REE/uranium deposits in the world, among 20 or so similar occurrences scattered around that island's non-glaciated margins. Other prospects are under development by a number of mining companies, including some from China.

While the island has made clear it is not for sale, its government is signalling it is open to business, particularly in the minerals sector. Earlier this year, Greenland's elections saw the ascendancy of the pro-business Demokraatit Party, which has promised to accelerate the development of the country's minerals and other resources. At the same time, the party's leadership is pushing back against Trump's rhetoric. If an opinion poll held in January this year is anything to go by, 85% of Greenlanders are against the island becoming part of the USA.

As a postscript, both the Greenland and Danish governments are aware of the need to protect and conserve the island's melting ice cap, which is recognised by research groups worldwide as a major control over global climates and sea levels. This in turn suggests a responsibility to consider the conflict posed by the potentially adverse environmental effects of unbridled mineral extraction and processing. Such issues will undoubtedly come to the fore if and when the islanders decide to hold the referendum on full independence that has been granted by Denmark.

(Editor's note: see also back-cover photo-montage together with extended captions on page 132)

Astrochronology: a new tool for ultra-precise age-dating

A novel approach to incorporating individual astronomical cycle durations into a conventional radioisotopic age-dating project has resulted in a well constrained age of 519.62 Ma (519.70–519.54 Ma) for the first occurrence of trilobites in West Gondwana. The researchers (Sinnesael et al, *Geology* 2024, doi.org/10.1130/G51718.1) claim that such a level of precision is exceptional for biological events in deep time, and could be the way forward for bracketing fossil ages in other sequences. The findings are based on detailed sedimentological cyclostratigraphical analysis of the lower Cambrian strata of Tiout, Morocco, which are characterised by regular alternations of darker limestones with paler-coloured marlstones, with individual beds and cycles traceable over many kilometres.

In this sequence, several orders of bundled cyclicity had been noted by other workers, including a basic ~5 m 'rhythm'; ~25 m 'cyclothems' consisting of several rhythms; ~100 m 'supercycles'; and a 'long-term trend'. However, this new research suggests that there is an *orbitally-instigated* eccentricity–precession origin of these cyclothems and rhythms, which indicates the operation in deep time of Milankovitch cycles (for a further explanation, see the article by Jon Lee in *Mercian Geologist* for 2011, pp 274–280). This type of recurrence has been deduced from detailed studies of the ratios between the thicknesses of the different cycles, expressed as the bundled sedimentary alternations. In particular, the rhythm/cyclothem thickness ratio of ~1:5–1:6 is close to the short- to long-obliquity duration ratio calculated by other researchers for the early Cambrian (Laskar, 2020; Farhat et al., 2022). The suggestion is that the changes reflect changes in sedimentation caused by orbital precession forcing of the monsoonal circulation. Such strong precession signals are most evident in low-latitude monsoon-dominated climatic regimes, hinting that this part of Gondwana occupied a low, rather than high, palaeolatitude; a conclusion that may inform the on-going debate about the configuration of Cambrian palaeocontinents.

The researchers do point out that while improving age estimates for biostratigraphic horizons, it remains crucial to also keep in mind geographic, environmental, and taphonomic controls on fossil occurrences. Overall, however, the study demonstrates the potential for using astrochronology, when combined with high-quality isotopic age-dating, to better constrain time-scales and major changes in other cyclic sedimentary sequences (such as the Coal Measures cyclothems?) well into deep-time.

Cyclic bundles, consisting of alternations between dark limestones and lighter marlstones in the Lie De Vin Formation, Morocco (Thanks to Matthias Sinnesael and Kilian Eichenseer for providing this image).