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Accumulation of rare earth elements in common vine leaves is achieved through extraction from soil and transport in the xylem sap

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Rare Earth Elements play a critical role in current clean technologies but face scarcity and environmental challenges in their extraction. Using semi-natural controlled experiments, we tested the ability of *V. vinifera* L. to accumulate Rare Earth Elements naturally present in the soil. We demonstrate that *V. vinifera* L. passively transports all Rare Earth Elements from soil to leaves via Xylem-sap mirroring soil conditions. Since this process starts from the fifth month of *V. vinifera L.* growth without damaging the crops, we. estimate that it is possible to recover 900 milligrams of Rare Earth Elements per hectares from vineyard without harvesting the whole plant. We propose the direct extraction of Rare Earth Elements from leaves overcoming unstainable biomass burning yielding environmental and economic benefits.

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Rare Earth Elements (REE) are central to the development and dissemination of clean energy technologies that enable the energy transition and contribute to a zero-carbon economy[1–3]. The REE group consists of 14 elements from $_{58}$Ce to $_{71}$Lu (Lanthanides series) associated with Y and La. All REE are characterized by a common outer electronic configuration, while each element has a different number of electrons in the 4f shell[4]. The fact that elements within the group are ordered according to the increasing number of electrons in their 4f orbitals, makes it possible to define two distinct REE groups: Light-REE (LREE, from La to Gd) and Heavy-REE (HREE, from Tb to Lu plus Y). LREE are primarily used in hybrid vehicles, some wind-energy applications, rechargeable batteries and cell phones[5,6] while HREE are essential in lighting and optical applications, magnetic resonance imaging and high-capacity energy storage[7–10]. Although it is undeniable that REE participate in furthering green technologies, their extraction generates intensive pollution resulting in environmental damage[11–15], not to mention human exploitation[16,17]. REE mining requires extraction processes, including strong acid leaching, which produce high amounts of liquid and solid toxic waste[18–20]. For example, in the Ganzhou region of China alone, it is estimated that to date, 190 million tons of toxic tailing waste have been deposited, 15,000 hectares of forest have been destroyed and hundreds of mines have been abandoned[21]. This calls into question the sustainability of current REE-dependant clean technologies. Furthermore, given the current geographic concentration of REE deposits, if REE supply is to be sustainable in the long term, we must identify alternative sources [22] as advised by the EU and the U.S. Department of Energy[23,24].

Current alternative sources to new mine extraction have focused on recycling and recovery of electronic and industrial waste, although the results have been disappointing[11,25–27]. Recently, high REE concentrations have been detected in seafloor sediment and deep-sea mud, which could potentially represent a new source of REE[28–30]. However, exploring the ocean floor for REE deposits is both expensive and time-consuming and mining the seafloor endangers the deep-sea ecosystem and biodiversity[11,31]. A second alternative source has been suggested, consisting of REE recovery from plants used for phytoremediation[32–36]. However, this process is currently used only for the heavily polluted soil of decommissioned mines, and therefore does neither provide a reliable long-term alternative source or solve the issue of geographic concentration.

Although not essential to plant growth, REE can be detected in plant tissues at moderate concentrations under non-contaminated conditions. Pioneering works have suggested that there may be meaningful REE uptake from roots to leaves in the case of *V. vinifera* L[37–40].

Therefore, we decided to investigate REE accumulation during the plant growth cycle, specific REE uptake and the influence of soil composition on the uptake in roots and leaves, in order to determine whether vineyards could be a sustainable source of recovered REE. We evaluated REE accumulation in *V. vinifera* L. for the entire REE series by analyzing the main potential REE reservoirs: substrates, roots, leaves as well as the xylem sap. Since REE and other substances are transported through the xylem[41,42], we sampled and analyzed the xylem sap composition at different stages of plant growth. In natural soils, the amount of accumulated REE depends on pristine rock and weathering conditions, in keeping with the Oddo-Harkins rule[43]. According to the Oddo-Harkins rule, the abundance of a given REE in soils decreases by 2–3 orders of magnitude as the element's atomic number increases. During the plant's growth cycle, the behavior of trace metals depends on both the element's specific chemical properties and its relative abundance[39,44–47]. While natural soils have a

known and constant REE abundance, that relationship is modified in artificially enriched soils where one or several elements are introduced. The modification of relative REE abundance may in turn change the potential reactivity of each REE.

Consequently, we investigated REE behavior in semi-natural and 'spiked' conditions, where the substrate was enriched by an equal-molar solution of REE, such that the spiked system had constant REE abundance throughout the series. This allowed us to evaluate the individual behavior of each REE during the complex transfer process from soil to leave. Experiments were carried out in a field laboratory of the Department of Agricultural, Food and Forestry Sciences (University of Palermo in Italy), using one-year-old *V. vinifera* plants, previously grown in sandy-clay soil. Pristine plants were transplanted in off-soil polyurethane pots with peat/cocoa fiber substrates with a low amount of REE and high levels of organic substances, mainly humic acid[48]. Pots were exposed to atmospheric agents (i.e., rain, wind) in our field laboratory, while irrigation was supplied using a micro-irrigation system without phytosanitary treatments[49]. It is challenging to carry out quantitative determination of REE at the trace or ultra-trace level in a low amount of solution. This was the case for xylem-sap determinations because the collected samples were in the range of 200–500 μL. We therefore developed specific strategies for data quality assurance as a function of the different matrices, as reported in Supplementary Information.

Results and discussion

The analytical results of the study are reported in Supplementary Data 1 and 2. Fig. 1 shows that the amount of major and minor metals and major organic acids present in the xylem sap remained constant during the time of investigation, both in control and REE enriched treatments. The data provided evidence that the artificial REE enrichment conditions of our experiment (spiked soil) did not substantially affect the physiology of xylem transport of these substances. The REE concentration in the different substrates reported in Fig. 2a revealed that under control conditions, REE abundance decreased by two orders of magnitude as a function of the atomic mass with a 'zig-zag' shape in agreement with the Oddo-Harkins rule[43,50]. However, under spiked conditions, REE abundance remained constant. This indicates that our experimental conditions discriminated between natural and artificially enriched substrates. To estimate the possible enrichment or depletion in single or groups of REE in the plant reservoirs, we normalized the amount of REE to the Upper Continental Crust abundance, UCC, using the following
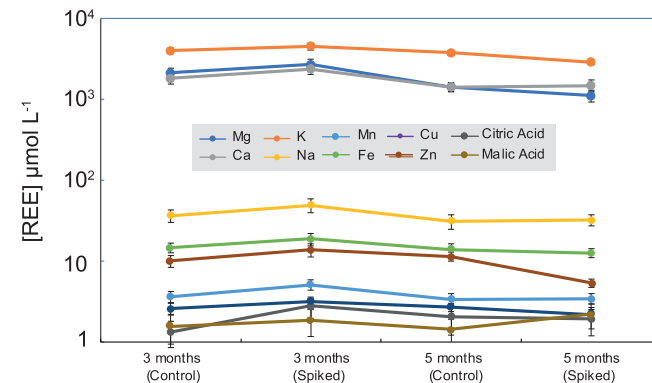
Fig. 1 Evolution of nutrients and organic ligands in Xylem-sap. Na, Mg, K, Ca (macronutrients), Fe, Mn, Cu, Zn (micronutrients) and organic ligands (citric acid, malic acid) in xylem sap during the growth of *V. vinifera* under control and spiked conditions. The error bars represent the standard deviation obtained from three independent measurements.
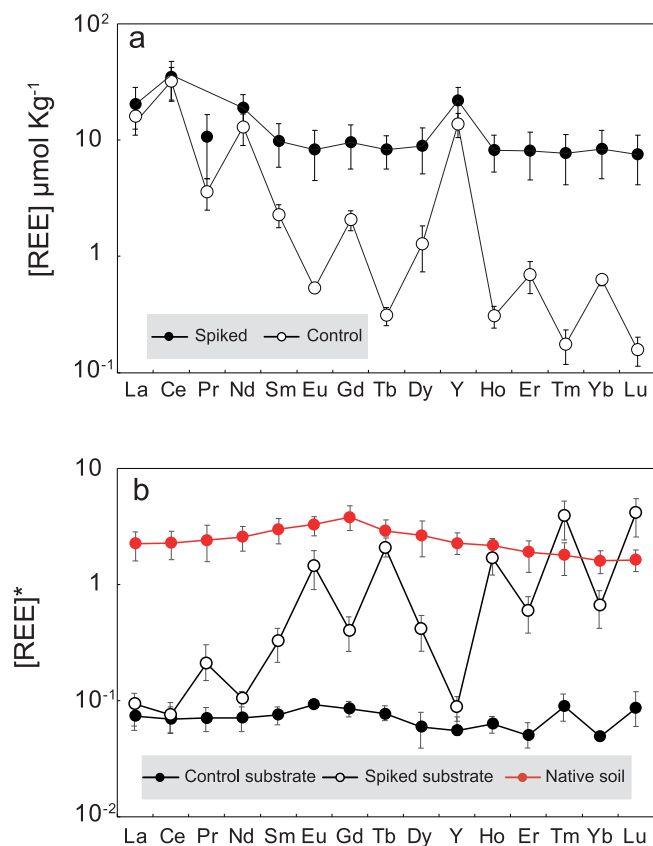
Fig. 2 Rare Earth Elements in native soil and experimental substrates. a Concentration of REE (μmol/kg) for control and spiked substrates. **b** REE* distribution in native soil, control and spiked substrates. The error bars represent the standard deviation obtained from three independent measurements.

Eq. (1)[38,39,43,50]:

$$REE^* = \frac{REE}{REE_{UCC}} \qquad (1)$$

Where REE* is the normalised value. Plotting the REE* as a function of the single REE for control, spiked and native soils (Fig. 2b), we found that native and control soils had similar spectra while the spiked substrate displayed a 'zig-zag' shape and a nonlinear enrichment of HREE compared to LREE. Our chart illustrates that native and control soils reflected natural conditions, whereas the spiked substrate reflected its artificial enrichment. The REE* in substrates, roots, xylem sap and leaves under control and spiked conditions are reported in Fig. 3. We found that at the 3rd month of growth, under control conditions, roots were slightly enriched in LREE compared to HREE, while they displayed a 'zig-zag' shape in spiked conditions. At this point in time, it appeared that root's REE* mirrored the substrate's REE* (Fig. 3a, b). However, in xylem sap and leaves, REE* remained constant in control and spiked conditions (Fig. 3c, d) indicating that REE uptake and transport were not modified through the plant's physiological process. At the 5th month of growth, xylem sap and leaves had a slight enrichment in LREE compared to HREE under control conditions, while they displayed a 'zig zag' shape under spiked conditions, mirroring the root's REE*. This suggests that, at this stage of growth, REE transport from roots to leaves through xylem sap did not notably fractionate REE, be they single or grouped. A notable exception in the REE series was Eu which displayed a positive anomaly in leaves but not in xylem sap and roots. The Eu anomaly in leaves may result from

photosynthetic reactions: in the aqueous xylem sap, REE should be trivalent, while redox photosynthetic reactions in the leaves may lead to bivalent Eu[51] that may substitute Ca[47,52], or form Eu-organic complexes (e.g. with proteins)[53,54]. Additionally, the more stable half-shell fill in f orbitals of Eu^{2+} generates greater ionic radii increasing similarities with alkaline-earth metals that enhance Eu mobility in the REE series[54,55].

The evolution of [∑LREE]/[∑HREE] ratio as a function of time (Fig. 4) shows that, under control conditions, the [∑LREE]/[∑HREE] ratio weakly decreased in roots and increased in leaves, indicating the preferential transfer of LREE over HREE in the aerial parts of the plant (Fig. 4a). Under spiked conditions, the ratio [∑LREE]/[∑HREE] slightly decreased as a function of time in both roots and leaves indicating that neither LREE nor HREE were preferentially transferred to leaves (Fig. 4b). The preferential uptake of HREE compared to LREE observed in roots, in both growth conditions, may result from the preferential HREE uptake into clays or carbonate minerals (Fig. 5) as previously observed in natural soils[44,56]. The preferential accumulation of HREE also mirrors the enhanced magnetic moment, dictated by the progressive filling of f-orbital along the REE series. We were, however, surprised by the differences in behavior we observed in leaves between control and spiked conditions. While under control conditions LREE enrichment in leaves reflected the ability of LREE to form stable complex ions with xylem sap organic molecules[54], no preferential enrichment was observed under spiked conditions suggesting that all REE behaved essentially in the same manner regardless of the plant's physiology. The process controlling REE uptake and sequestration in plants is still object of discussion[57]. A model based on the intracellular acidity of roots assumes that after selective absorption of REE as trivalent cations, these are fixed in roots by co-precipitation of rare earth ions-salts such as insoluble oxalates or phosphates[58–60]. However, this model does not account for differences in abundance throughout the REE series[43,44]. It is problematic to establish effective REE fractionation throughout the soil/plant system under natural soil conditions, where REE can vary by one or two orders of magnitude. Our spiked experiment minimized such differences and highlighted the individual REE chemical behavior during the transfer from soil to leaves. Our results show that *V. vinifera* passively transports all REE into plant tissues reflecting their mutual ionic similarity[61]. We have demonstrated that REE transport in *V. vinifera* allowed accumulation in leaves mirroring the soil conditions. In *V. vinifera* REE soil content was the most important factor affecting their bioavailability, as reported for other vascular plants[62].

Implications

The results of our study reveal that *V. vinifera* was able to take up REE dispersed in soils and accumulate them in leaves, starting from the initial vegetative growth stage. We observed this process both for plants cultivated in soils with natural REE abundance and in artificially enriched soils. To evidence the process, we used Coryell-Masuda plots, i.e. the normalised expression REE* (on a logarithmic scale) compared to the atomic number or ionic radius (on a linear scale). We found that irrespective of abundance conditions, plant organs and substrates had similar spectra, indicating that REE transport was not selective in *V. vinifera* but rather depended on the relative abundance of REE in the growth substrate. Our study shows that there were no relevant anomalies in *V. vinifera* xylem sap.

Given that the amount of REE accumulated in leaves is a direct function of the soil's REE content, the REE amount in leaves can be easily estimated. We found that after a three-month growth period, leaves growing in the control substrate accumulated
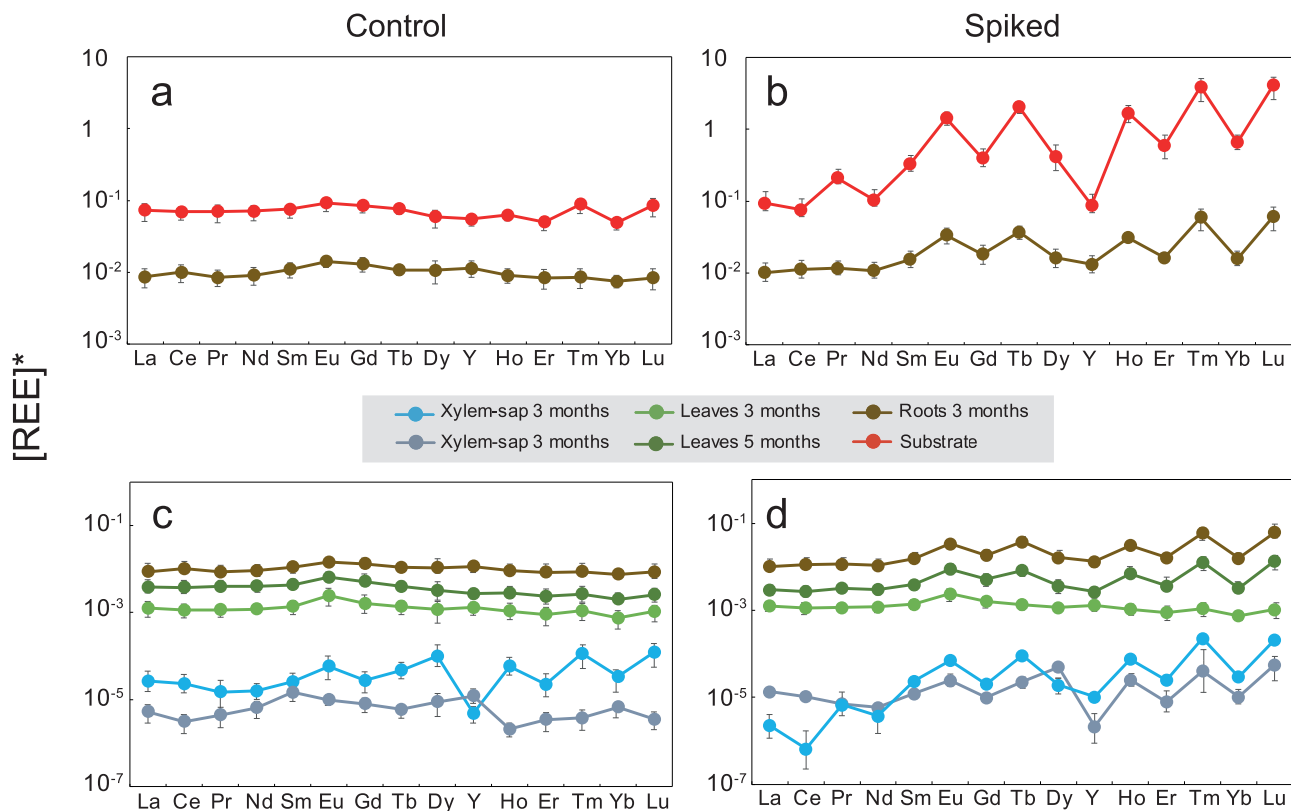
Fig. 3 Rare earth elements distribution in substrates, roots xylem-sap and leaves. a REE* of Substrate and Roots under control conditions at 3 months. **b** REE* of Substrate and Roots under Spiked conditions at 3 months. **c** REE* of Roots, Xylem-sap and Leaves under control condition at 3 and 5 months. **d** REE* of Roots Xylem-sap and Leaves under Spiked condition at 3 and 5 months. The error bars represent the standard deviation obtained from three independent measurements.
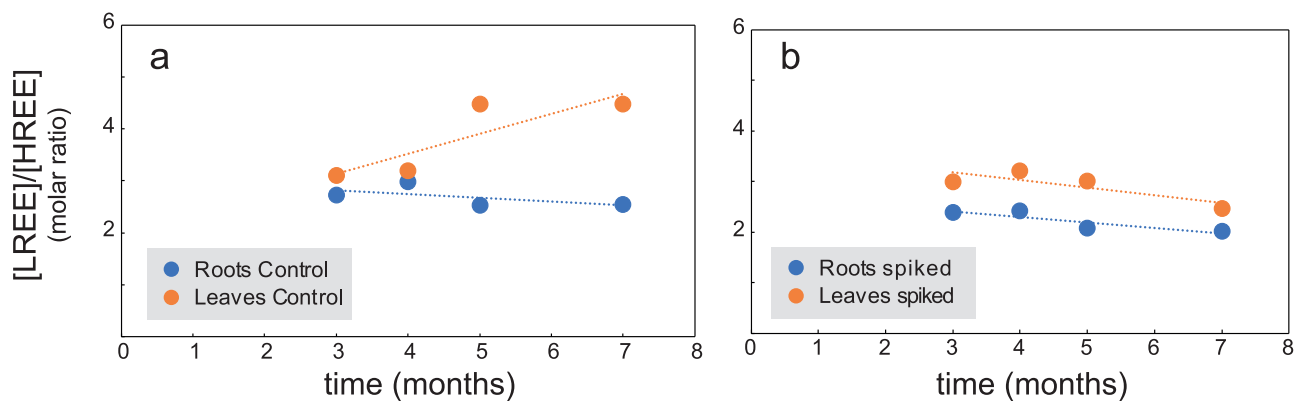
Fig. 4 Ratio of light and heavy rare earth elements in roots and leaves. $\sum$LREE/$\sum$HREE ratio(mol/kg) in Roots and Leaves under control conditions (**a**) and spiked conditions (**b**). (The error bar is within the range of the individual data points).

430 µg/kg (dry weight) of REE, corresponding to 345 µg/kg of LREE and 85 µg/kg of HREE. Assuming an overall average leaf weight of 0.5 kg per plant (dry weight) and a typical density of 4000 plants per hectare (ha), we estimate that it is possible to recover by 900 mg/ha of REE (i.e., 730 mg of LREE and 170 mg of HREE). Data on REE levels in *V. vinifera* cultivations are fragmented, varying from 118.41 µg/kg for vineyards on carbonate soils[63] to 2061 µg/kg on volcanic soils[64], corresponding to a recovery of 236.80 mg/ha and 4121.90 mg/ha respectively. REE recovery from vineyards does not pose any environmental concern compared to the use of transgenic plants in phytoremediation strategies[65]. Since grapevines generate new foliage each year,

harvesting and treatment of *V. vinifera* leaves could represent a regular, sustainable source of REE. Several strategies have been proposed for REE recycling from electronic and catalysts wastes, slag, ashes, biomass from tailings[33,35,66–68] adopting pyro- and hydro-metallurgy or bio-metallurgy technologies[69]. However, these technologies have several drawbacks. Pyro-metallurgical methods, for instance, are poorly selective, high-energy consuming, produce harmful gases and require expensive apparatus[70]. Hydro-metallurgy, despite having higher selective recovery rates and low harmful gas emissions, generates sludge and corrosion[66]. Bio-metallurgy is promising for its environmental friendliness and reasonable costs, though it needs long
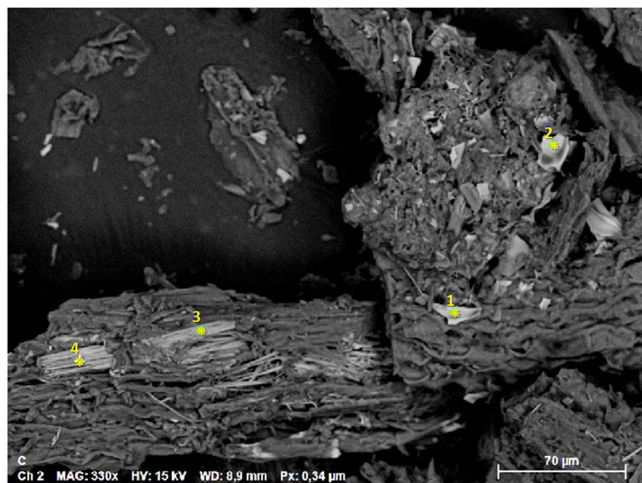
Fig. 5 Scanning electron microscopy of roots. SEM image (Back-Scattered Electron Detector) of the *V. vinifera* root texture. Points 1 and 2 are clay aggregates. Points 3 and 4 are Ca-carbonate minerals.

operation times and has low efficiency. The recovery of REE mixtures by direct extraction, without burning the plant, has been recently developed[34,71,72]. REE extraction from biomass is obtained by extracting solutions (i.e., H_2SO_4, citric acid or an EDTA), with an efficiency greater than 70% for citric acid[73]. This acid is widely recognized for its environmental sustainability and is used in food industry[74]. Extraction procedures are a sustainable method today and are directly applicable in wineries, where citric and tartaric acids are commonly used in the winemaking process. Leaves of *V. vinifera* could be harvested and processed by installing an organic acid bath in the winery, allowing REE extraction with negligible costs and environmental impact.

REE recovery from *V. vinifera* leaves is economically feasible when compared to other secondary sources obtained by phytomining. Although the economic feasibility evaluation of REE recovery is influenced by commercial and political perspectives[75,76], extraction of REE from *V. vinifera* leaves requires neither initial investment costs nor new plantations. In addition, leaf supply from vineyards does not need additional agronomic practices, thus reducing possible initial capital expenses (e.g. pollution survey, land preparation, irrigation system, roads, incineration equipment), labor costs (e.g. seedling, ploughing, fertilizing, insect and weed control), materials costs (e.g. hyperaccumulator seedlings; farm chemicals) water and electricity costs[77]. We have estimated economic savings greater than 70% compared to managing a phytoremediation implant. In addition, during phyto-mining plants are harvested and burned leading to SiO_2, Al_2O_3 residual ash[78]. Extraction of REE from amorphous aluminosilicate matrix needs dissolution and/or leaching by strong acid (HNO_3 or H_2SO_4) with high extraction costs, CO_2 emission and solid wastes[75]. Separation technologies using organic acid solutions have very low energy and extraction costs, as no incineration is needed[73]. The proposed strategy is also compliant with the circular economy model of production, as leaves are unexploited materials becoming renewable resources. Leaves are abundant, low-cost and provide a continuous source of REE throughout the entire life cycle of the vineyard. We therefore propose *V. vinifera* plants as a secondary source of REE, since vineyards cover over 7 million hectares worldwide representing a huge natural REE reservoir that, in the current economic, technological and geostrategic context, constitute a important potential alternative source.

Conclusions

In this study, we have explored the possible use of *V. vinifera* leaves as a novel alternative source of REE. Using semi-natural controlled experimental conditions, we found that *V. vinifera* can accumulate REE from vineyard soils. We observed that REE accumulated naturally in leaves in function of the amount of REE present in the soil, irrespective of growth conditions. Our results show that xylem-sap passively transports all REE into leaves, while roots preferentially retain Heavy-REE, and Light-REE accumulate in leaves without damage for the crop. We have estimated that it is possible to recover 450 µg of REE per kg of leaves without harvesting the whole plant or using new land, avoiding new investments and without using chemicals (e.g., pesticides, fertilizers) or greenhouse production. Therefore, vineyards represent a potentially abundant, sustainable and low-cost source of REE supply compatible with energy saving and environmental friendly criteria. We propose a simple solid/liquid REE extraction from *V. vinifera* leaves using weak acids as complexing agents, avoiding currently used biomass burning practices. The challenge is to consider vineyard leaves as a small but continuous, efficient, and sustainable source of REE throughout the entire life cycle of *V. vinifera*.

Methods

Experimental system. Pristine plants (one year old) grown in native clayey sandy soil were transplanted in off-soil polyurethane pots with peat/cocao ratio of 2:3 w/w (control substrates). We chose two different experimental growth conditions: one using 1 kg of control substrate and a second using the same substrate artificially spiked with 12.5 µmoL/Kg of the entire range of REE (Spiked Substrate). The REE-spiked solution (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) was prepared by diluting standard solutions (1000 mg/L, pH <1) of each element to 0.05 mM in high purity water yielding an initial working solution with a pH close to 5.6. We assumed that, under such initial conditions, REE may be in the state of free ions. The whole experimental system consisted of 16 plants: 4 from control soil and 12 from spiked soil, each sampled three times. Sampling was carried out at 3, 4, 5 and 7 months for soil-substrate, roots, xylem-sap and leaves. The native soil was sampled at the beginning of the experiment.

Sample preparation. Nitric acid (65%) and hydrogen peroxide (30%) ultrapure reagents (Merck, Milan Italy) were used throughout the study. A standard solution containing REE and the internal standard (rhenium) of 1000 ± 5 mg/L were purchased from BDH and CPI International. Ultrapure water at 18.2 MΩ cm was produced by an EASYpureII (Thermo, Milan Italy) ion-exchange system. Native soil and substrate were dried at 105 °C, gently crushed, and sieved (Ø 0.5 mm) and an aliquot of 250 mg was transferred to PFA microwave vessels. Leaves and roots were chopped, dried at 105 °C for 24 h and ground in an agate mortar. An aliquot of 500 mg of leaves and 250 mg of roots were successfully transferred to PFA microwave vessels. All samples were digested in a closed Mars Xpress microwave (CEM, Bergamo Italy), with 4.5 ml of 2:1 v/v mixture of HNO_3:H_2O_2. The temperature was initially increased from 20° to 200 °C in the first ten minutes and then to 200 °C for 50 min. After digestion, samples were quantitatively transferred into graduated polypropylene tubes and diluted with ultrapure water (dilution was to 10 ml for leaves and 100 ml for native soils, substrates and roots). Blanks were carried out using an ultrapure water solution.

Xylem sap extraction. The xylem sap was collected using the vacuum-chamber method[79]. One or two shoots per plant were rapidly defoliated with a razor blade and removed. A ring of bark was removed from the apical end of the shoot to avoid phloem contamination. The cut surface was rinsed with distilled water and blotted dry, while the shoot was forced through a rubber stopper. The apical end was inserted into a plastic vial, sealed with sealing film and placed inside a Buchner flask. The plastic vial was immersed in an ice bath to reduce evaporation of xylem sap during extraction. After connecting the flask to a vacuum pump and applying a pressure of −0.08 MPa for 30 s, segments of approx. 2 cm in length were cut off starting from the basal part of the shoot. At the end of the extraction, the vial was sealed and stored for further analysis. About 200–250 µL of sap was collected from each shoot.

Chemical measurements. The Agilent Technologies 7500ce Series Spectrometer by ICP-MS was selected for REE determinations adopting the following operative conditions: power 1550 W, nebulizer gas flow $1.00\,l\,m^{-1}$, auxiliary gas flow $0.85\,l\,m^{-1}$ and plasma gas flow $15\,l\,m^{-1}$. Acquisition time was 180 s for every determination while three replicates were performed using the ^{7}Li, ^{59}Co, ^{89}Y, ^{140}Ce, and ^{205}Tl isotopic masses with a minimal precision of 2%. REE

Table 1 Summary of our experimental mass spectrometry conditions.

Analyte	Quantification transition (m/z)	Qualification transition (m/z)	Cone voltage (CV)	Collision Energy (CE)
Citric acid	191 > 87	191 > 111	20	15
Lactic acid	89 > 43		15	10
Malic acid	133 > 115	133 > 71	15	10
Succinic acid	117 > 73	117 > 99	15	10

determinations were accomplished by measuring ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{151}Eu, ^{158}Gd, ^{159}Tb ^{163}Dy, ^{89}Y, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu isotopic masses while ^{187}Re served as the internal standard. Possible formation of oxides and doubly charged ion interferences were verified by the CeO^+/Ce^+ and Ce^{2+}/Ce^+ ratios and found to be systematically lower than 0.5%. Isobaric interferences, related to Eu isotopes (^{151}Eu, ^{153}Eu), were evaluated using polyatomic BaO^+ ions ($^{135}Ba^{16}O^+$, $^{137}Ba^{16}O^+$) via the certified INCT-OBTL-5 Oriental Basma Tobacco Leaves standard and Ba concentration. Possible Ba interference on Eu determination was evaluated by measuring ^{135}Ba concentration in all samples. We found that the (Ba/Eu) ratio was constantly lower than 200[80]. The Xylem-sap composition was also analyzed by measuring both macronutrients (MAN) and micronutrients (MIN) for ^{26}Mg, ^{39}K, ^{43}Ca and ^{56}Fe, ^{55}Mn, ^{55}Mn, ^{63}Cu, ^{66}Zn, isotopic mass measurements.

Anomalies or fractionations of a group or an individual REE relative to the others were estimated using the following Eq. (2):

$$REE/REE_{UCC} = \frac{\left(\frac{REE_{organs}}{REE_{UCC}}\right)^2_i}{\left[\left(\frac{REE_{organs}}{REE_{UCC}}\right)_{i+1} + \left(\frac{REE_{organs}}{REE_{UCC}}\right)_{i-1}\right]} \qquad (2)$$

where the subscript "organs" correspond to the REE concentration in the roots, leaves and xylem sap. The subscript "i" indicates every REE of the series, whereas "(i + 1)" and "(i − 1)" are immediate neighbors, before and after within the series[37,39].

Organic-acid determinations were performed by high-performance liquid chromatography with detection in mass/mass spectrometry, HPLC-MS/MS, system (Waters Alliance- Micromass Quattro Micro, Waters, USA), using a Synergy Hydro-RP column (250×4.6 mm with 4 µm particles from Phenomenex Torrance, CA, USA) to separate citric, lactic, malic and succinic acids under isocratic conditions. Other instrumental conditions included: mobile phase water with 0.15% formic acid/methanol (95:5); injection volume of 20 µL; a flow rate of 0.4 ml/min; column temperature of 30 °C; MS/MS-Ionization mode with negative-ion electrospray ionization (ESI-); capillary voltage of 2.5 kV; source temperature 120 °C; desolvation temperature 400 °C; cone gas flow 50 l h^{-1}; desolvation gas flow 800 l h^{-1}; collision cell pressure 3.5×10^{-3} mbar and dwell time 0.1 s. We used the Multiple Reaction Monitoring (MRM) mode for data acquisition. Mass transitions are reported in Table 1 while quantification was carried out using external calibration curves in the range of 0.1–1.0 mg l^{-1}.

Data quality assurance. Quantitative determination of REE at the trace or ultra-trace level, in a low amount of solution, is challenging. This was the case for xylem sap because the collected samples were in the range of 200–500 µL. We consequently developed specific strategies for data quality assurance as a function of the different matrices. Specific details for both validation and quality control plans were reported in Supplementary Information. In this work, only data from processes under control were used, making the results repeatable and referable.

Data availability
Supplementary Data 1 and 2 are available at this repository: https://doi.org/10.6084/m9.figshare.23803815 Supplementary Data 1 includes the results of macronutrients, micronutrients, and organic ligand analysis in Xylem-sap. Supplementary Data 2 includes the results of REE analysis in native soil, substrates, root xylem-sap, and leaves.

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Author contributions

M.B., P.Z and F.S. designed this study; M.B. and P.Z wrote the manuscript with contributions from and F.S. and D.P; M.B. F.S. and E.O. collected the samples and performed the experiments; P.C. F.L.and E.O. participated in the interpretation and discussion.

Competing interests

The authors declare no competing interests.

Additional information