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Extractive Waste as a Resource: Quartz, Feldspars, and Rare Earth Elements from Gneiss Quarries of the Verbano-Cusio-Ossola Province (Piedmont, Northern Italy)

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Abstract: The growing demand for raw materials requires the optimization of extractive processes and innovative approaches, such as the recovery of quarrying and processing waste. Waste materials from gneiss (ranging from blocks up to residual sludge) used as dimension stone (*Beola* and *Serizzo* from Piedmont, northern Italy) were characterized for chemistry, mineralogy, and petrography: quartz and feldspars (plagioclase and K-feldspar) are the most abundant minerals, followed by micas (biotite and minor muscovite) and traces of chlorite and epidote (allanite). Quartz and feldspars could be reused in the industrial minerals sector, especially in the ceramics industry; depending on the purity requirements of the raw materials, some mica separation treatments may be required. The most critical issues relate to the small grain size and the relative abundance of mica in some commercial varieties. The presence of allanite opens new possibilities for the recovery of rare earth elements (REE, critical raw materials).

Keywords: quarry; waste; gneiss; quartz; feldspars; REE

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1. Introduction

Raw materials (RM) and critical raw materials (CRM) are crucial for modern society. The United Nations Sustainable Development Goals [1], as well as the implementation of the Paris Agreement, resulted in the vast utilization of a wide range of minerals for green technologies, such as low-carbon applications [2]. Among RM, dimension stones (marbles, granites, and stones) represent, at the EU level, a very important market. Dimension stone quarrying is characterized by an international market, and it involves high commercial prices on average, which can balance the high production costs typically faced by quarrying companies.

Some general characteristics of dimension stone extraction have to be faced to guarantee a profitable and sustainable quarrying activity: the variability of the lithotypes; the physicomechanical properties and the mineralogical and geochemical composition of the rock mass; the relatively limited productions of commercial blocks (due to the structural characteristics of the deposit); and the low ratio between the "workable" and the whole volumes extracted, with a consequent huge production of extractive waste (EW). Also important are the geographical position of the deposit and the geomorphological conditions of the quarry, which influence the accessibility and logistics for exploitation and transport, as well as the intrinsic value of the exploited materials (e.g., compared to the similar rocks coming from non-EU countries). All the quoted features affect the choice of the exploitation techniques and technologies to be employed and, on the other side, the choice of the best procedures to manage and (hopefully) recover the EW volume produced during the exploitation activities. Furthermore, during both the planning and the management activities, to boost the stone resources exploitation and ensure the best environmental compatibility, it is more and more pertinent to search for an increasing ratio of the extracted material which, even if unusable for ornamental purposes, may be fruitfully exploited as "secondary" raw material (SRM) in other sectors: the circular economy applied to the extractive industry [3,4].

Extraction also requires planning: where and how to cut to minimize waste. The ratio between the blocks above a minimum volume and the total rock extraction determines the quantity of waste to be relocated or, better, re-used. EW management is still a matter of concern; indeed, in 2018 the mining and quarrying industry represented the second most important sector in terms of waste quantities produced in the EU-27 (26.6% or 562 Mt), after Construction and Demolition Waste (CDW—36% or 769.32 Mt; [5]). At present, these materials are managed in different ways, both locally and at the EU level.

The necessity to reduce the use of non-renewable natural resources and, at the same time, to minimize the negative impacts the on environment, has led to an increasingly high interest in recovering and recycling. Nevertheless, the principles to minimize waste production and to reuse/recycle waste materials are parts of the EU policy expressed in the Europe 2020 strategy for a resource-efficient Europe and the EU Strategy for Sustainable Development [6].

Quarry and EW management needs the interaction of private and public bodies, composed, on the one hand, of industries which invest in dimension stone exploitation and in treatment activities to produce new recycled products from EW and, on the other hand, of different levels of governance, citizenship, research and education, improving capacities, techniques, models, and cooperation structures among stakeholders (at the regional, transnational, and European level) for the territorial deployment of the circular economy.

Extractive waste (including residual sludge) can potentially be recovered for different, yet tested, applications (Figure 1), such as:

- Aggregate for infrastructures, building, and civil works [7–10];
- Industrial minerals [4,11];
- Artificial substrates for environmental rehabilitation [12–14];
- Geopolymers [15–17];
- Filler for industry [18–20];
- RM and CRM [21,22].

In this paper, we show the example of an important Italian quarrying district that is a source of *Beola* and *Serizzo*, two varieties of gneiss extracted in the Verbano-Cusio-Ossola (VCO) province (Piedmont, Western Alps). In particular, the extractive waste coming from *Serizzo* and *Beola* could represent a potential resource from which to exploit quartz and feldspar for the ceramic sector and even has potential for the extraction of rare earths (REE).

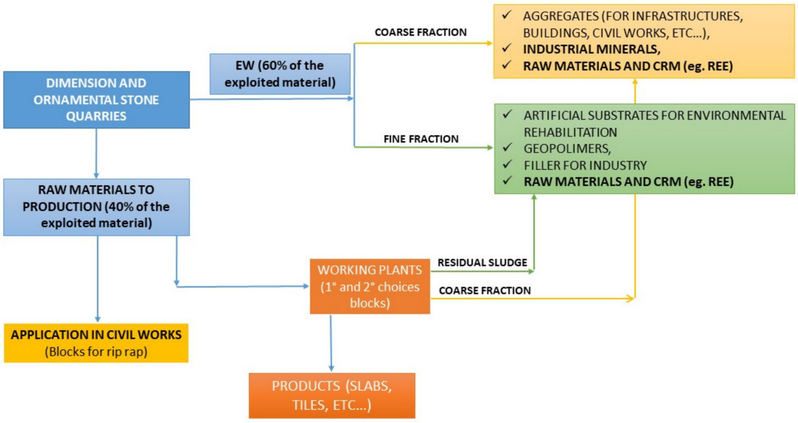

Figure 1. Simplified flow diagram about potential recovery of EW from dimension stones. 1st (1°) and 2nd (2°) choice referred to the quality of blocks.

2. Materials and Methods

2.1. Beola and Serizzo: Quarries, Dimension Stones, and Waste Materials

The Verbano-Cusio-Ossola (VCO) area, together with the *Pietra di Luserna* district, has the most important active quarrying districts in Piedmont (northern Italy) and is among the most significant in Italy [23]. In 2017, 72 quarries for dimension stone exploitation were active in the Piedmont region, with an estimated production of about 1,016,091 t/y (406,890 m^3/y). In 2005, the total number of dimension stone quarries was 112, with an estimated production of about 1,284,996.50 t/y (509,218.57 m^3/y) [24]. The VCO quarries are located at altitudes which swing between 300 and 1300 m above sea level (a.s.l.); thanks to the particular geology of the area (Figure 2), which represents a natural section of the main Alpine tectonic units, numerous lithologies are exposed and, consequently, many different stone materials: granites (Baveno and Mergozzo), *Beola* gneiss (Vogogna, Trontano, Beura-Cardezza, Villadossola, and Montecrestese), *Serizzo* gneiss (Premia, Formazza, Crodo, and Crevoladossola), and marbles (Crevoladossola, Ornavasso, and Candoglia). The VCO dimension stones, because of the morphology (medium to high mountain areas), are mostly exploited in mountainside quarries [25]. *Beola* and *Serizzo*, two different gneiss varieties, marketed with different commercial names, represent the most important dimension stone resource in 33 out of 48 quarrying sites [26,27]. *Serizzo* and *Beola* are foliated (in some cases also lineated) orthogneisses, quartz-felspathic metamorphic rocks (granitic to granodioritic protolith), deriving from different Penninic units (also Austroalpine in the southernmost part), reflecting the complex structural and metamorphic evolution of the Alpine nappes (Figure 2). Although they derive from different structural units, from the lithological point of view they are very comparable (orthogneisses with granitic to granodioritic protolith) and have undergone the same metamorphic evolution (albeit with different degrees of deformation) [28]. Their mineralogical composition is comparable (quartz, plagioclase, K-feldspar, biotite, and white mica), but the main differences lie in the fabric and microstructure (grain size and shape, planar and linear anisotropies): *Serizzo* is moderately foliated, with a gneissic to augen texture, whereas the *Beola* varieties are characterized by strong mylonitic foliation (and therefore easily split into thin slabs) [26,27]. Both stone materials are extracted in large opencast quarries (Figure 3) through the combined use of diamond wire and explosive (detonating cord). It is also important to highlight the strong decrement from 2005 to 2017 in terms of the *Serizzo* and *Beola* production, decreasing from 401,460.30 t/y (150,435.55 m^3/y) in 2005, to about 184,801.47 t/y (69,922.64 m^3/y) in 2017 [24]: a huge decrement in terms of production, linked to the crisis in the building sector and competition from foreign materials.

The percentage of EW from VCO quarry sites represents about the 60% of the total exploited material: this percentage (estimated by local producers and quantified by annual topographical surveys and the assessment of annual net productions [24]) is in line with the EW production from siliceous dimension stones at the Italian level. As for *Serizzo* and *Beola*, it is possible to estimate an EW production of about 110,880 t/y (41,954 m^3/y of shapeless blocks and rock chips). Together with the EW coming from quarry exploitation, another important waste, whose management is very challenging (not only at the Italian level), is represented by residual sludge (EWC 010413, European Waste Code 010413, wastes from stone cutting and sawing other than those mentioned in 010407). Sludge production at the VCO level is estimated at about 17,700 t/y (after filter-pressing) [29].

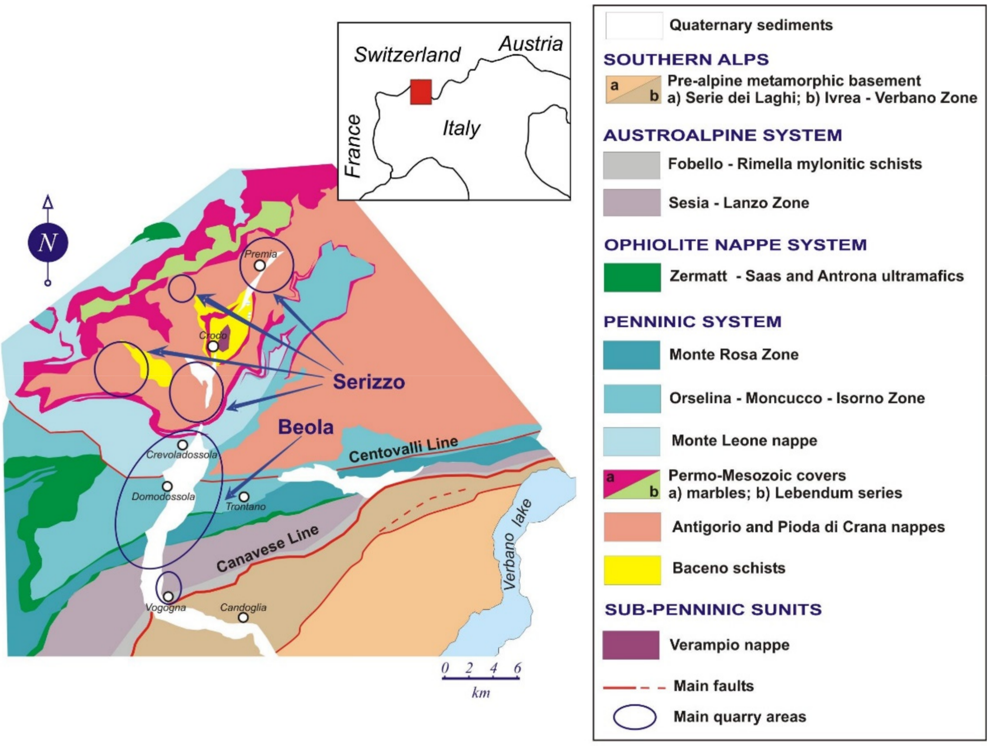

Figure 2. Simplified geological sketch map of the VCO area, focused on the *Serizzo* and *Beola* quarrying areas.

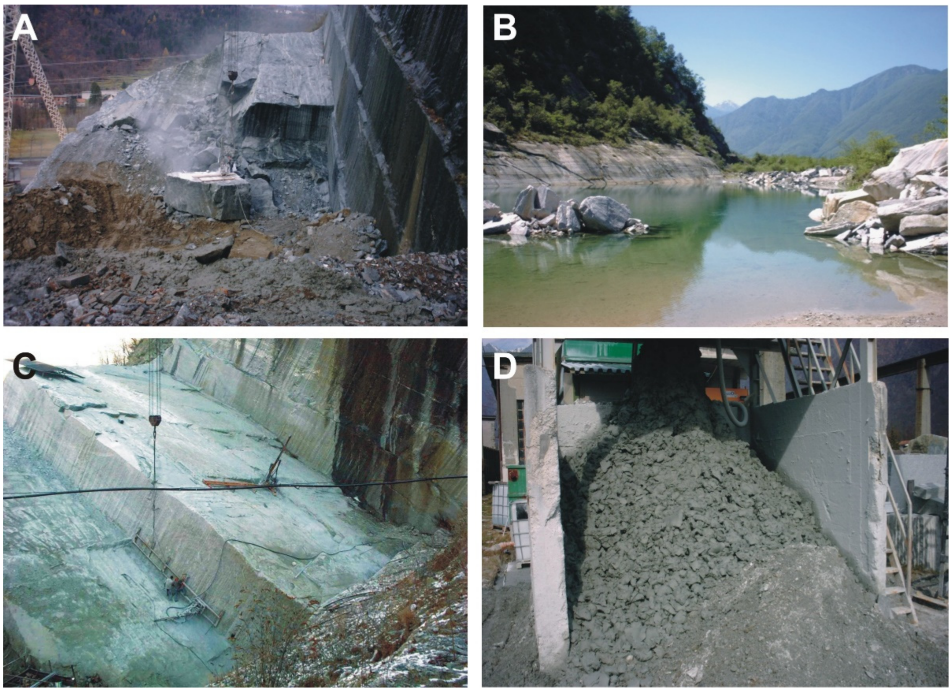

Figure 3. (**A**) *Serizzo Antigorio* quarry near Crodo; (**B**) abandoned *Beola* valley bottom quarry near Beura-Cardezza; (**C**) *Serizzo Formazza* quarry with inclined benches; (**D**) Filter-pressed residual sludge deriving from stone processing facilities.

The VCO quarrying area is also important for a peculiar EW recovery from granite quarry sites; indeed, feldspar and quartz have been exploited since 1995, exploiting ancient granite EW facilities (in 1995, there were 2 authorized extractive sites; at present, there are 5) [4]. The feldspar and quartz production from granite waste was estimated at about 181,017 t/y (83,506 m^3/y) in 2017; it was 565,674.00 t/y–257,124.55 m^3/y in 2005. Granite waste is ground, screened, and selected through two steps of Nd-Fe-B roll magnetic separation: biotite (virtually the only Fe-containing mineral in granite) is separated to obtain a quartz–feldspar mix with a low FeO_{tot} content (<0.15 wt.%), which is optimal for the ceramic sector (porcelain stoneware) and is used, for example, in the important district of Sassuolo (Emilia-Romagna, Italy). This is a virtuous example of reuse of quarrying waste as a secondary raw material (SRM) with high added value.

As stated before, *Serizzo* and *Beola* are quartz–felspathic metamorphic rocks (orthogneisses, from granitic to granodioritic protolith), which show similar mineralogical and petrographical characteristics when compared to local granites. Thus, EW deriving from *Serizzo* and *Beola* could be exploited for quartz and feldspar (and REE). The present paper aims at characterizing the mineralogy, geochemistry, and petrography of such waste (from quarrying and processing activities) to state if and how, by planning focused processing activities (planned but not completely carried out at a laboratory level), it is possible to exploit RM and CRM from them.

2.2. Sampling and Analytical Procedures

A total of 220 samples (115 *Beola* and 75 *Serizzo* waste rock chips, with a mass of 700–900 g each, and 30 residual sludges), was collected between 2013 and 2021 in 42 different quarries (33 active and 9 dismissed), favoring the most commercially used and common materials. It must be remembered that the *Beola* varieties, especially, show a certain compositional variability, particularly in the southernmost area (near Vogogna, Figure 2). The aim is to evaluate the chemical and mineralogical qualities of the materials and to reuse them in the industrial (and ore) mineral sector.

All of the samples were characterized by polarized light microscopy (PLM) on thin sections, X-ray powder diffraction (XRPD), and scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray spectrometer (EDS); grain size was assessed both by PLM and SEM. From 130 samples investigated by thin-section textural analysis, 52 were selected for microprobe work; the rock-forming minerals were analyzed with an electron probe microanalysis (EPMA) in wavelength-dispersion mode (WDS). The whole-rock geochemistry was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS); C and S were quantified by LECO®. The powders for the XRPD and whole-rock geochemistry analyses were obtained by crushing with a hydraulic press and subsequent grinding in an agate ball mill to an optimum particle size (<10 μm). For the PLM and SEM analysis, as well as for EDS and WDS EPMA, polished thin sections (30 μm thickness) were prepared.

The PLM analyses (Leica DME 13595 microscope, Leica, Düsseldorf, Germany), both in the transmitted and the reflected light mode, were performed on polished thin sections; point counting was carried out on rock-forming minerals for quantitative analysis. The XRPD analyses were performed using a PANalytical X'Pert PRO PW3040/60 X-ray diffractometer with Ni-filtered Cu Kα radiation at 40 kV and 40 mA, $\frac{1}{2}\circ$ divergence and receiving slits, and a step scan of 0.02° 2θ in the 3–80° 2θ range; the limit of detection of XRPD is approximately 0.5 wt.%. The qualitative phase analysis was performed using the PANalytical HighScore Plus software version 2.2c, using the ICSD PDF2-2008 database; the quantitative phase analysis was carried out running the FULLPAT software [30]. The quantitative phase analysis was calibrated and verified on pure phases mixtures (quartz, plagioclase, K-feldspar, biotite, muscovite, and chlorite) in known ratios. The mineralogy and microstructures were also assessed by SEM (Vega TS Tescan 5163 XM, Tescan Vega, Huntsville, TX, USA) in combination with an EDS analyzer (EDAX Genesis 400, EDAX, Mahwah, NJ, USA), with 200 pA and 20 kV as standard conditions, on carbon-coated samples. The quantitative mineral chemistry was performed on plagioclase, K-feldspar, and allanite using a Jeol JXA-8200 EPMA-WDS; the system was operated with an accelerating voltage of 15 kV, a beam current of 15 nA, and a counting time of 60 s on peak and 30 s on backgrounds, using a series of minerals as standards (omphacite for Si and Ca; kaersutite for Al, K, Na, and Ti; fayalite for Mg; spessartine for Fe and Mn; and bastnäsite and monazite for REE). The results were processed for matrix effects using a conventional Φ(ρZ) routine in the Jeol software. Th whole-rock geochemistry was assessed for major elements (ICP-AES, whole rock fusion with meta-borate), trace and rare earth (RE) elements (ICP-MS), and C and S (LECO®, St. Joseph, MI, USA) at the Chemistry Labs, Vancouver (Canada).

3. Results

3.1. Whole-Rock Geochemistry

The chemistry of the *Serizzo* and *Beola* orthogneisses from the Penninic nappes evidences a quite homogeneous composition, typical of a granitic to granodioritic protolith, a peraluminous character, and a calcalkaline affinity (Table 1). A compositional gap is observed in the Monte Leone nappe rocks: two different groups are present, one between 62 and 66% and the other between 70 and 78% of SiO_2. On the contrary, the orthogneisses of the Monte Rosa nappe and Orselina-Moncucco-Isorno Zone [23,31] have a more homogeneous chemical composition and a small silica variation: 70–75% and 70–73%, respectively. The major and trace elements are well correlated with SiO_2, except for Na_2O and K_2O, which cluster around the values of 3% and 5%, respectively. Only a few lithotypes extracted in the southernmost zone (Vogogna area and Fobello-Rimella schists) differ from these relatively homogeneous trends, due to some basic lithologies (prasinites), which are currently no longer quarried. The REE patterns (Figure 4) show enrichment in light REE (LREE) over heavy REE (HREE), mainly La_N/Yb_N = 4–20, and an incompatible behavior for LREE with increasing SiO_2 contents; the more evolved rocks of the Monte Rosa nappe are LREE-depleted.

Table 1. Whole-rock geochemistry by ICP-OES and ICP-MS (C and S by LECO®) of *Serizzo* and *Beola* (115 *Beola* and 75 *Serizzo* waste rock chips, median values and range, wt.%).

	***Serizzo* (Median)**	***Serizzo* (Range)**	***Beola* (Median)**	***Beola* (Range)**
SiO_2	67.82	65.32–71.21	72.68	57.35–75.49
TiO_2	0.29	0.19–0.41	0.24	0.02–1.09
Al_2O_3	17.21	15.85–18.33	14.43	12.81–15.38
Fe_2O_3	1.35	0.85–1.74	1.90	0.39–6.88
MnO	0.18	0.09–0.25	0.17	0.01–0.11
MgO	0.74	0.41–1.05	0.47	0.21–5.16
CaO	3.25	2.86–3.86	1.22	0.72–7.06
Na_2O	3.39	2.85–4.06	3.58	2.89–7.09
K_2O	3.12	2.67–4.11	4.28	0.39–5.93
P_2O_5	0.19	0.14–0.36	0.17	0.11–0.26
LOI	1.2	0.5–1.9	0.7	0.4–2.7
C	0.02	0.01–0.07	0.03	0.01–0.13
S	0.06	0.01–0.18	0.05	<0.01–0.13
ΣREE * (ppm)	379	125–520	174	101–320

* Includes Y.

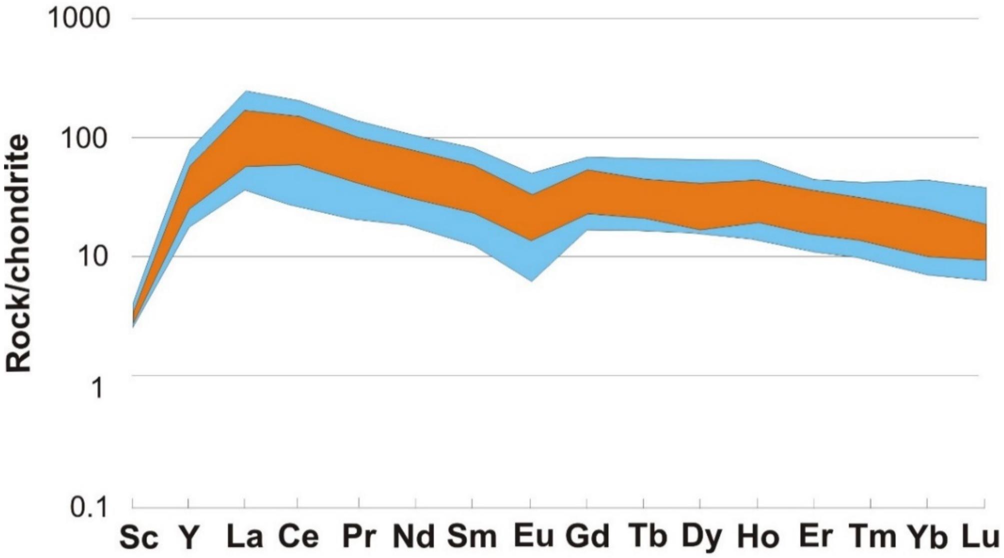

Figure 4. Rock/chondrite normalized spidergram [32,33] of the Serizzo (orange) and Beola (light blue), based on 190 samples.

The composition of the residual sludge essentially reflects the composition of the processed lithotypes, with the slight increases in Co, Cu, Cr, and Ni content being attributable to the wear of the cutting and polishing tools.

3.2. Mineralogy and Petrography

Beola and Serizzo are quartz–feldspathic rocks, with a relatively monotonous mineralogical composition: quartz, plagioclase, K-feldspar (orthoclase and/or microcline), biotite, minor muscovite, and chlorite; a typical accessory mineral is allanite (or orthite), a REE-bearing epidote-group mineral [34]. The abundance of the main rock-forming minerals is reported in Table 2.

Table 2. Mineralogical composition of *Serizzo* and *Beola* (mean values and range of 190 samples, wt.%), determined by quantitative XRPD and OM (point counting).

	***Serizzo* (Mean)**	***Serizzo* (Range)**	***Beola* (Mean)**	***Beola* (Range)**
Qtz	35.1	28.2–35.6	40.6	14.3–52.2
Pl	30.2	28.2–36.4	27.1	21.1–32.5
Kfs	19.2	15.1–23.7	16.3	5.6–26.1
Bt	9.5	4.3–16.1	8.1	2.2–12.3
WM	4.2	1.9–8.6	5.3	3.5–15.4
Chl	1.8	0.8–3.2	2.6	2.5–9.6

Qtz = quartz; Pl = plagioclase; Kfs = K-feldspar; Bt = biotite; WM = white mica (muscovite); Chl = chlorite.

The Serizzo varieties have a medium grain size (typical range 250–1400 μm, K-feldspar up to 2.5 cm), a generally marked planar foliation, and an augen texture (partially recrystallized K-feldspars, e.g., Figure 5). Microcline occurs as large grains in the less-foliated varieties, and the crystals are generally perthitic; in rare cases, it is possible to note small grains of included plagioclase. The plagioclase is generally present as two generations: the first generation is represented by subhedral crystals of oligoclase with inclusions of muscovite, clinozoisite, and biotite, whereas the second is represented by polygonal aggregates, sometimes of albitic composition. Muscovite, sphene, zircon, clinozoisite-epidote, often with allanite nuclei, are almost constantly present in the biotite aggregates in a very close association, whilst opaques and monazite are generally absent. Zircon is present as an inclusion in biotite and allanite. The different abundances of biotite are responsible for the different shades of the materials: in the darker ones, the abundances are always greater than 8 wt.%.

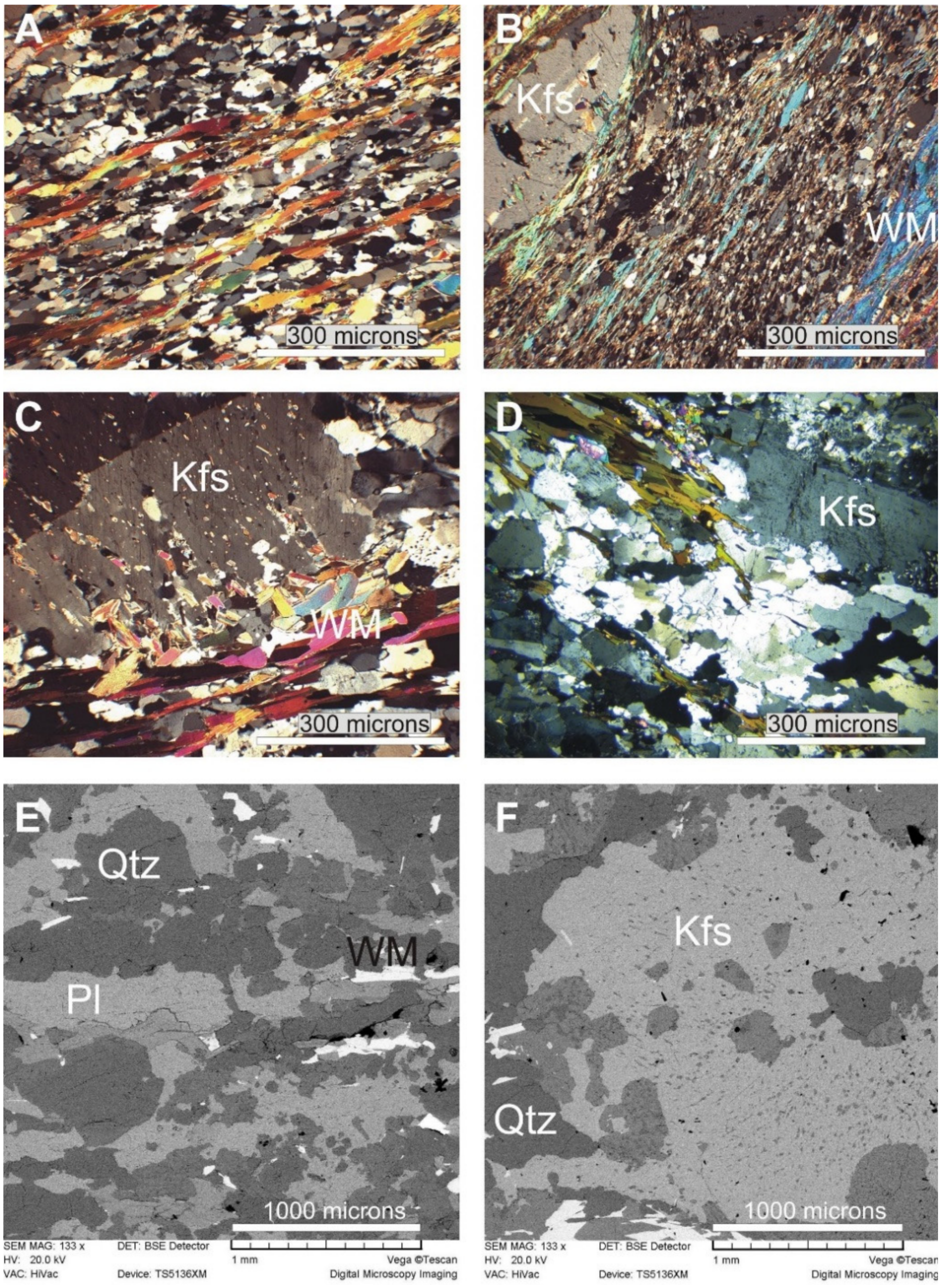

Figure 5. (**A**–**D**): polarized light micrographs (crossed polars) of Beola (**A**,**B**) and Serizzo (**C**,**D**) varieties. (**E**,**F**): SEM back-scattered electrons micrographs of Beola (**E**) and Serizzo (**F**). Qtz = quartz; Pl = plagioclase; Kfs = K-feldspar; WM = white mica.

Similarly to Serizzo, the Beola varieties contain quartz, K-feldspar (microcline), plagioclase (oligoclase and widespread albite), biotite, and white mica (muscovite), although in different proportions (Figure 5) and with smaller grain size (typical range 50–750 µm, K-feldspar up to 3–4-mm). The difference among the different varieties is due to the different rock fabric and to the presence or absence of specific accessory or secondary minerals. The varieties from the Monte Rosa nappe (Figure 2) are fine-grained and characterized by a strong mineralogical lineation, mainly due to the white mica and tourmaline alignments. Biotite is rare, and K-feldspar is porphyroclastic, locally dissected by microfaults. The varieties deriving from the other Penninic units differ mainly due to the different amounts of white mica, chlorite, and epidote (clinozoisite and allanite). The most marked differences concern the varieties quarried in the southernmost area (Fobello Rimella schists, Figure 2); these are the varieties with the finest grain size, mylonitic foliation, and greater abundance of phyllosilicates (biotite, muscovite, and chlorite). A variety currently no longer quarried (Verde Vogogna) shows a mineralogical composition referable to a metabasite (prasinite). The abundance of allanite in both Beola and Serizzo, estimated from point counting in PLM and SEM images in backscattered electrons, can be estimated to be between about 0.3 and 0.7 wt.%.

For residual sludge, most particles have a grain size <80 μm (typical range 8–45 μm), with slight variations attributable to the cutting tools used (e.g., diamond disk, multi-blade gangsaw, sander, and polisher). Traces of metal grit (cast iron and steel) are found and are due to the use of the multi-blade gangsaw.

3.3. Mineral Chemistry

The mineralogical composition of plagioclase and K-feldspar is reported in Tables 3 and 4, respectively. Quartz is the most abundant mineral, appearing in deformed polycrystalline aggregates and sometimes in lenses and rods. In both the Serizzo and the Beola varieties, plagioclase has an anorthite content of between 24 and 30% (oligoclase). The plagioclases of the first generation show an average anorthite content slightly but constantly higher than that of the unzoned grains of the polygonal aggregates; more evident is the difference in composition between the relict plagioclase and the reverse-zoned plagioclase of the new generation. In both Serizzo and Beola, in the latter to a greater extent, plagioclase crystals of albitic composition are present. K-feldspar (up to 2 cm in length in Serizzo) is mainly microcline and to a lesser extent orthoclase; marginal granulation is a common character, and the sub-grains are non-perthitic and often associated with mirmekitic plagioclase. In the more foliated Serizzo varieties, the K-feldspar builds up lenses of granoblastic aggregates consisting of non-perthitic and undeformed microcline and oligoclase with traces of quartz.

Table 3. Mineral chemistry of *Serizzo* and *Beola* plagioclase (median values and range, core, wt.%). Ab = albite; An = anorthite; Or = orthoclase.

	***Serizzo* Pl (Median)**	***Serizzo* Pl (Range)**	***Beola* Pl (Median)**	***Beola* Pl (Range)**
SiO_2	62.05	61.65–63.87	64.94	63.51–65.33
TiO_2	<0.01	<0.01–0.02	<0.01	<0.01–0.05
Al_2O_3	23.51	22.82–23.94	20.97	20.68–22.14
FeO	0.10	0.05–0.17	0.08	0.03–0.21
MnO	<0.01	<0.01–0.02	<0.01	<0.01–0.06
MgO	<0.01	<0.01–0.05	0.01	<0.01–0.14
CaO	5.19	4.68–5.42	4.12	3.88–5.21
Na_2O	8.36	7.88–8.47	9.44	7.96–10.12
K_2O	0.54	0.37–0.71	0.36	0.26–0.62
Total	99.75		99.92	
Number of ions calculated on the basis of 8 O				
Si	2.761		2.873	
Ti	0.000		0.000	
Al	1.233		1.093	
Fe^{2+}	0.003		0.003	
Mn	0.000		0.000	
Mg	0.000		0.001	
Ca	0.247		0.195	
Na	0.721		0.810	

Table 3. *Cont.*

	***Serizzo* Pl (Median)**	***Serizzo* Pl (Range)**	***Beola* Pl (Median)**	***Beola* Pl (Range)**
K	0.030		0.020	
Total	4.997		4.995	
Ab%	72.17		78.97	
An%	24.76		19.05	
Or%	3.07		1.98	

Table 4. Mineral chemistry of *Serizzo* and *Beola* K-feldspar (median values and range, core, wt.%).

	***Serizzo* Kfs (Median)**	***Serizzo* Kfs (Range)**	***Beola* Kfs (Median)**	***Beola* Kfs (Range)**
SiO_2	64.83	63.89–66.97	64.54	63.65–65.84
TiO_2	0.01	<0.01–0.06	<0.01	<0.01–0.09
Al_2O_3	19.18	18.35–19.87	19.57	17.23–20.23
FeO	0.07	0.02–0.18	0.12	0.04–0.32
MnO	<0.01	<0.01–0.05	<0.01	<0.01–0.08
MgO	0.02	0.01–0.09	0.04	0.01–0.10
CaO	0.18	0.09–0.34	0.16	0.03–0.50
Na_2O	0.96	0.75–1.27	0.74	0.60–2.52
K_2O	14.70	13.65–15.60	14.67	11.79–15.24
Total	99.95		99.84	
	Number of ions calculated on the basis of 8 O			
Si	2.978		2.966	
Ti	0.000		0.000	
Al	1.038		1.060	
Fe^{2+}	0.003		0.005	
Mn	0.000		0.000	
Mg	0.001		0.003	
Ca	0.009		0.008	
Na	0.085		0.066	
K	0.860		0.860	
Total	4.976		4.967	
Ab%	8.95		7.06	
An%	0.93		0.84	
Or%	90.13		92.10	

Biotite is virtually the only Fe–Mg mineral of the Serizzo and Beola varieties; amphiboles are very rare (hornblende and traces of tremolite–actinolite). The composition of biotite is homogeneous within the single lamella, and the composition of the different lamellae of an aggregate is almost the same (<1 wt.% variation in FeO and MgO content, TiO_2 content ranging from 1.65 to 2.76 wt.%). Muscovite contains small amounts of Fe and sometimes minimal traces of Mn. Epidote is a characteristic accessory mineral for both Beola and Serizzo, and it is possible to distinguish three different occurrences: small clinozoisite grains within plagioclase; epidote or clinozoisite xenoblasts in the quartz–feldspar aggregates, and large grains or idioblasts with an allanite core in close association with biotite and sphene. Allanite shows a progressive decrease in Fe content from the core to the periphery; Th and U are present in traces, and the total rare earth oxides (REO) content is $\geq$ 20.0 wt.%. The typical composition of allanite (core) is reported in Table 5. The allanite idioblasts (e.g., Figure 6) are the product of a complex metamorphic reaction (probably through step reactions) involving the transformation of the igneous iron-rich biotite into a more Mg-rich type; the released Fe^{2+} reacted with monazite and clinozoisite to give allanite. When all the La, Ce, and Fe^{2+} were consumed, epidote began to crystallize around allanite, taking all the available Fe^{3+} [35–37]. Monazite-Ce is another REE-bearing mineral (e.g., Figure 6D) although very rare and occasional, especially in Serizzo varieties.

Table 5. Mineral chemistry of allanite (median values and range, core, wt.%).

	Aln	Range
Sio_2	35.21	33.76–35.86
TiO_2	0.08	0.05–0.13
ThO_2	0.86	0.55–1.38
Al_2O_3	19.54	17.35–20.65
FeO	7.85	6.65–12.14
MnO	0.05	0.02–0.12
MgO	0.16	0.08–0.31
CaO	14.04	12.21–16.18
Y_2O_3	0.32	0.21–0.50
La_2O_3	3.67	2.86–5.12
Ce_2O_3	9.32	6.89–12.24
Pr_2O_3	1.21	0.82–1.95
Nd_2O_3	4.36	3.54–5.68
Sm_2O_3	0.67	0.34–1.11
Na_2O	0.04	0.02–0.10
K_2O	0.05	0.03–0.12
Total	97.43	
	Number of ions calculated on the basis of 25 O	
Si	6.350	
Ti	0.011	
Th	0.076	
Al	4.153	
Fe^{2+}	1.184	
Mn	0.008	
Mg	0.043	
Ca	2.713	
Y	0.031	
La	0.244	
Ce	0.615	
Pr	0.079	
Nd	0.281	
Sm	0.042	
Na	0.014	
K	0.011	
Total	15.854	

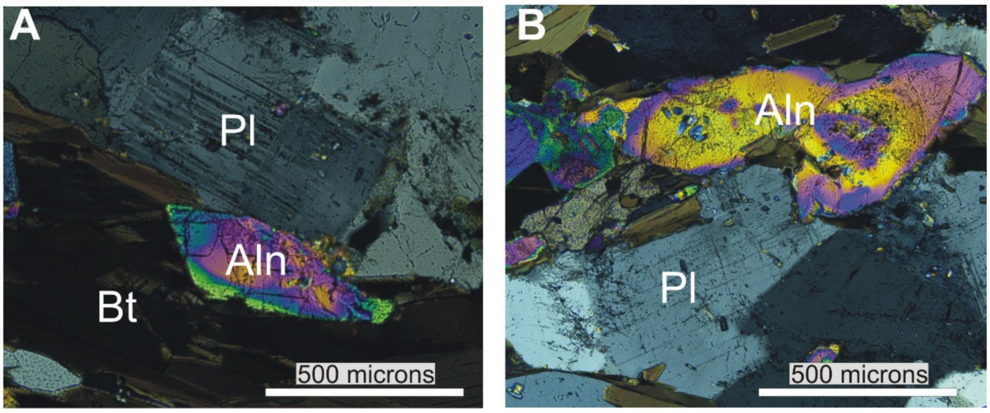

Figure 6. *Cont.*

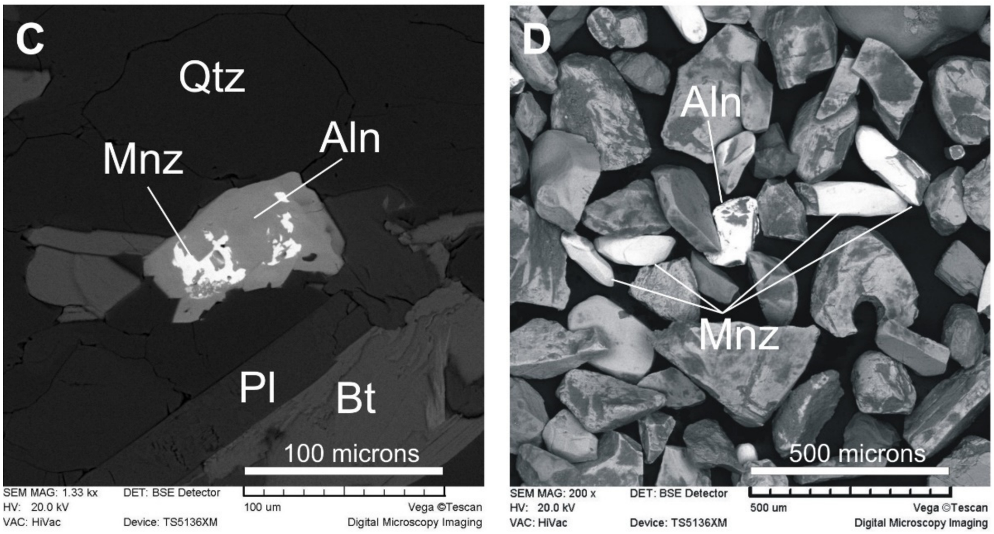

Figure 6. (**A**,**B**): polarized light micrographs (crossed polars) of allanite (Aln) within Serizzo varieties. (**C**): SEM back-scattered electrons micrograph of allanite with monazite (Mnz) inclusions. (**D**): SEM back-scattered electrons micrograph of monazite and allanite crystals within residual sludge deriving from dimension stone processing. Pl = plagioclase; Qtz = quartz; Bt = biotite.

4. Discussion

The various analytical investigations carried out on the *Serizzo* and *Beola* waste revealed chemical and mineralogical compositions of potential interest. In the same extractive district, granite waste has been successfully recovered for years [4]; after the magnetic separation of biotite, a quartz–feldspar mix is obtained that is perfectly suitable for the ceramic sector, especially porcelain stoneware ($FeO_{tot} \leq 0.15$ wt.%). As orthogneisses are the product of the metamorphism of granitoid rocks, they may potentially have the same applications in the industrial minerals sector [38]. However, compared to the non-metamorphic protoliths, there are several factors that make the operation more complex: first, the grain size is smaller, especially for *Beola* varieties, followed by the greater abundance of phyllosilicates (biotite and muscovite). A further critical point is represented by the microstructures: the marked foliation (especially for *Beola*) and the greater complexity of the intergranular contacts (metamorphic recrystallization), as well as the presence of K-feldspar porphyroclasts with the inclusions of other minerals. To achieve optimal separation of the individual mineralogical phases, more extensive crushing would be required. *Serizzo* and *Beola* feldspar's compositions are theoretically suitable (with a low Fe content) for the ceramic and feldspar industry [38], and virtually, the only Fe-bearing mineral is biotite. After crushing to an optimum size to achieve mineral separation, biotite can be separated using conventional magnetic separation techniques [39], while muscovite would require innovative flotation techniques [40,41]. The level of treatment and abatement of FeO_{tot} will obviously depend on the final use: the most stringent parameters concern porcelain stoneware and granite ceramics, while ceramics with relatively high water absorption (e.g., wall tiles) do not require raw materials that are particularly low in FeO_{tot} [42]. As far as *Beola* is concerned, the least suitable varieties are those extracted in the southern area (Vogogna and Fobello-Rimella schists), due to the extremely minute grain size, the mylonitic texture, and the greater abundance of phyllosilicates, as well as the presence of basic lithotypes (in any case very subordinate). The most suitable lithotypes of *Beola* are instead those extracted in the Beura–Cardezza surroundings (Monte Rosa nappe), due to the particularly low FeO_{tot} content (*Beola Bianca*) and the lower abundance of biotite and muscovite. Greater mineralogical and textural homogeneity is observed for Serizzo, and the coarser-grained varieties (e.g., *Serizzo Antigorio*, the most common commercial variety) are certainly the most suitable. Regarding REE content, it should be noted that allanite contains virtually all the REEs of the lithotypes of concern. The REO content of allanite is $\geq$20 wt.%

(especially Ce_2O_3), which makes it an interesting minor mineral for REE extraction [43] and references therein]. As a heavy mineral (3.4–4.2 g/cm^3 [34]), it can be easily separated by conventional gravitational processes (e.g., shaking tables), without even requiring excessive rock comminution, by virtue of its grain size (500–150 μm). Gravimetric concentration would also allow the concentration of other accessory minerals, e.g., zircon and traces of monazite-Ce (an additional REE mineral, although very scarce in *Serizzo*). The feasibility of recovering *Serizzo* and *Beola* waste would require the opening of a pilot plant with crushing and screening processes and gravimetric and magnetic separation; the proper separation of materials in the processing plants is also very important in order to avoid a contamination with extraneous lithologies (e.g., marbles). As for the residual sludges, given their very fine grain (on average under 100 μm), it is very unlikely that they can be used to extract quartz and feldspar, but they are certainly suitable for the concentration of heavy minerals (e.g., allanite, zircon, and monazite).

5. Conclusions

The availability of raw materials and critical raw materials is increasingly under pressure, and the criticality of the processing infrastructure and the recovering of these elements from various resources leads the EU to be dependent on their imports, often from non-EU countries, which have always been affected by the fluctuating policies of the market, potential conflicts, higher environmental impacts connected to their exploitation, processing, and waste management. Several studies show that in many regions, massive amounts of strategically important materials, such as ore and industrial minerals, have piled up in extractive waste facilities and landfills [44]. This study precisely shows the importance of an in-depth knowledge of the “extractive waste” material; its exploitation could bring important benefits for the supply of essential industrial minerals in the ceramic sector, reducing imports and the economic and environmental costs related to transport. This already works very well with granites, whereas with gneisses more technical effort will be needed, but the potential and the quantities are there; the exploitation of quarrying and processing waste would also significantly reduce the material in landfills. Also to be considered is the use in ceramic sectors that are less stringent with regard to FeO_{tot} content: e.g., wall tiles, bricks, and other ceramics with relatively high water absorption. The presence of REE in potentially exploitable and easily concentrated ore minerals represents an important discovery of a new resource of a strategic raw material. The systematic recovery of extractive waste should significantly contribute to both land and environmental protection and to the safety of the quarries and the supply of raw materials.

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