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Detrital orthopyroxene as a tracer of geodynamic setting:: A Raman and SEM-EDS provenance study / Borromeo, L.; Ando, S.; Bersani, D.; Garzanti, E.; Gentile, P.; Mantovani, L.; Tribaudino, M. - In: CHEMICAL GEOLOGY. - ISSN 0009-2541. - 596:(2022), p. 120809.120809. [10.1016/j.chemgeo.2022.120809]

Availability: This version is available at: 11381/2922789 since: 2024-11-13T17:01:14Z

Publisher: Elsevier B.V.

Published DOI:10.1016/j.chemgeo.2022.120809

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Detrital orthopyroxene as a tracer of geodynamic setting: a Raman and SEM-EDS provenance study

Short title: Detrital orthopyroxene as provenance tracer

Laura Borromeo^{1*}, Sergio Andò¹, Danilo Bersani², Eduardo Garzanti¹, Paolo Gentile³, Luciana Mantovani², Mario Tribaudino⁴

* Correspondence to: University of Milano-Bicocca, Piazza della Scienza, 4, 20126, Milano (Italy) E-mail: laura.borromeo@unimib.it

¹Laboratory for Provenance Studies, Department of Earth and Environmental Sciences, University of Milano-Bicocca, 20126, Milano (Italy)

² Department of Mathematical, Physical and Computer Sciences, University of Parma, Parma,

43124, (Italy)

³ Platform of Microscopy, Department of Earth and Environmental Sciences, University of Milano-Bicocca, 20126, Milano (Italy)

⁴ Department of Earth Sciences, University of Torino, 10124, Torino, (Italy)

ABSTRACT

Raman spectroscopy is a powerful tool that for its efficiency is being used more and more frequently in high-resolution provenance analysis. In this study, dedicated to Ca-poor orthorhombic pyroxene, we focused on 15 samples of modern sands representing a full range of rock units exposed at different structural levels of continental, arc, or oceanic lithosphere and generated in diverse geodynamic settings. By coupling optical observations, SEM-EDS minerochemical and Raman spectroscopy analyses on the same grains we show how orthopyroxene from mantle, deep crustal, and volcanic rocks ranging in composition from andesite to dacite and felsic differentiates can be robustly distinguished. The Mg# [Mg/(Mg+Fe)] content of orthopyroxene grains can be accurately estimated by recording the characteristic position of their six main characteristic peaks (v_1 to v_6 , vibrational modes) even during routine point-counting under the Raman spectroscope. Most useful at this regard is the position of the strong and narrow v_3 peak (~655 cm⁻¹) that also allows to estimate Ca content if compared with the position of other peaks (especially v_1 , ~330 cm⁻¹). High-Mg orthopyroxene is exclusively derived from mantle rocks, whereas metagabbros of the lower continental crust and gabbroic rocks of the arc crust could be distinguished by their lower Ca.

The lowest Mg# was recorded in detrital orthopyroxene derived from the silicic Amiata Volcano in central Italy, whereas trachytes in rift-related settings did not show peculiar characteristics apart from their slightly higher Ca content.

Key Words: Provenance analysis; Enstatite; Hypersthene; Raman Spectroscopy; SEM-EDS chemical analyses; Volcanic orthopyroxene.

1 **1. Introduction**

2

3 In the last years, multi-method approaches to provenance analysis have provided a bounty of 4 information on sedimentary systems, improving our understanding of physical and chemical processes that control the modification of provenance signals during sediment transfer from source 5 6 to sink (Garzanti, 2016; Basu, 2017; Caracciolo, 2020). Techniques focusing on specific detrital 7 minerals or mineral groups have resulted to be particularly fruitful and exploited (Mange and 8 Morton, 2007; von Eynatten and Dunkl, 2012; Guo et al., 2020). Zircon played the lion's share 9 (Gehrels, 2011) and attentions were primarily dedicated to the composition of durable species, 10 including rutile (Meinhold, 2010), tourmaline (Guo et al., 2021), apatite (O'Sullivan et al., 2020), 11 garnet (Suggate and Hall, 2014), or Cr-spinel (Hu et al., 2014). Less specific attention was 12 dedicated to less durable ferromagnesian minerals (e.g., Lee et al., 2003; Andò and Garzanti, 2014; 13 Liang et al., 2019). This is largely because diagenized ancient sandstones generally contain only 14 those species that better resist intrastratal dissolution, whereas amphiboles and especially pyroxenes 15 and olivine are seldom preserved in ancient sandstones (Morton and Hallsworth, 2007; Garzanti et 16 al., 2018). The durability of detrital minerals, however, may also represent a disadvantage, because 17 grains can be easily recycled from one sedimentary cycle to the next thus loosing all information on 18 the routing of detritus (Andersen et al., 2016; Pastore et al., 2021). Conversely, where preserved, 19 less durable ferromagnesian minerals such as pyroxene are likely to be first cycle and thus able to 20 deliver information pointing directly to their igneous or metamorphic source-rocks (Cawood, 1983; 21 Caracciolo et al., 2016).

This modern-sand provenance study contributes to fill the existing knowledge gap concerning the distribution of pyroxene species in sediments, with the main aim to assess the relationship between pyroxene composition and the lithology of source rocks generated in diverse geodynamic settings. Here we shall focus on the simpler Ca-poor orthorhombic orthopyroxenes (OPX), whereas the much more complex relation between clinopyroxene composition and Raman spectra will be tackled in separate articles.





Figure 1. Comparison between traditional (upper panel; Poldervaart and Hess, 1947) and IMA (lower panel;
 Morimoto et al., 1988) orthopyroxene classification schemes. En: enstatite; Fs: ferrosilite; Wo: wollastonite.

32 In the traditional classification scheme (Poldervaart, 1947), orthopyroxenes were classified based 33 on their Mg/(Mg+Fe) atomic ratio (Mg#), as enstatite, bronzite, hypersthene, Fe-hypersthene, 34 eulite, or ferrosilite (Fig. 1). The current nomenclature of the International Mineralogical 35 Association (IMA), instead, more simply distinguishes between enstatite s.l. (Mg# > 0.5) and 36 ferrosilite s.l. (Mg# < 0.5) (Morimoto et al., 1988). Magnesium-rich orthopyroxene (enstatite s.s.) 37 characterizes ultramafic rocks (e.g., harzburgite, orthopyroxenite, kimberlite; Eggler, 1986; 38 Rezvukhin et al., 2019), and occurs in magnesian skarn and achondrite (Skridlaite et al., 2019; 39 Lorenz et al., 2020). Instead, iron-bearing orthopyroxene (hypersthene s.l.), characterizes 40 anorthosite (Morse, 1975), tonalite, monzonite (Leslie et al., 2003), andesite (Francalanci et al., 41 2005), and more felsic lavas and pyroclastic rocks (Aoki, et al., 1989), and occurs in granulite (Jan and Howie, 1980) or meteoritic chondrite (Kubovics et al., 2004). Iron-rich orthopyroxene (Mg# < 42 43 0.3) is rare in rocks, and pure ferrosilite very rare (Bowen, 1935, Lindsley, 1965) with a few 44 crystals identified in meteorites (Gismelseed et al., 2005).

45 In sedimentary petrography, it is common use to distinguish only two categories of orthopyroxene: 46 the nearly colourless, optically positive magnesium-rich orthopyroxene (enstatite s.s.; Poldervaart, 47 1947) from strongly pleochroic, optically negative iron-bearing orthopyroxene (hypersthene s.l., 48 including bronzite, hypersthene, and Fe-hypersthene; Tröeger, 1979; Mange and Maurer, 1992). 49 The correct determination of pyroxene species by both optical and electron-beam methods may 50 however represent a challenge (Dunkl et al., 2020 p.18). A full objective discrimination among 51 orthopyroxenes of different chemical composition is generally impossible under the microscope, 52 and small grains lacking colour or cleavage, or showing high roundness, alteration, or unusual 53 birefringence and interference figures may even be misidentified as epidote or olivine.

54 These difficulties can be overcome by obtaining decisive information with Raman spectroscopy, a 55 simple-to-perform technique that, in a few seconds and with no additional sample preparation,

56 allows us to achieve a robust mineralogical characterization (e.g., Griffith, 1969; Hope et al. 2001; 57 Bersani et al., 2009). Grains can be successfully identified even down to the size of a few microns 58 (Delmonte et al. 2017; Borromeo et al. 2018), also obtaining semi-quantitative crystallographic and 59 chemical information. This non-destructive technique is excellently suited to investigate minerals 60 and mineral inclusions (Raman, 1928; Griffith, 1969; Frezzotti et al. 2012), the specific lattice 61 features of which are readily revealed by their direct link with Raman peak positions. In the case of 62 vicariance, the different characteristics of the replacing ions produces variations in the strength and geometry of chemical bonds, and such differences in mineral structure are mirrored in Raman 63 64 spectra (Kuebler et al. 2006; Borromeo et al., 2017; Bersani et al. 2018). Preliminary investigations 65 on synthetic and selected natural pyroxenes have shown that chemical and structural changes can be 66 modelled by Raman spectroscopy in both orthorhombic and monoclinic pyroxenes (e.g., Tribaudino 67 et al., 2019; Stangarone et al., 2021).

68 In a multi-technique approach we combine optical, Raman spectroscopy, and SEM-EDS 69 minerochemical analyses conducted on the same grains not only to increase the robustness of 70 precise orthopyroxene identification but, especially, to establish the relationships among optical 71 properties (e.g., pleochroism and birefringence), chemical composition (e.g., relative amounts of 72 Mg, Fe, and Ca), and Raman signature (i.e., position of principal and secondary peaks) of detrital 73 orthopyroxene. Specifically, we aim to demonstrate how Raman spectroscopy can be routinely used 74 in high-resolution heavy-mineral analysis to efficiently assess the chemistry of pyroxene grains and 75 thus obtain reliable information on the lithology of source rocks (e.g., peridotite, gabbro, andesite, 76 dacite) and precious hints on the most plausible lithogenetic process (i.e., intrusive, effusive, or 77 metamorphic) and geodynamic environment in which it took place (e.g., ophiolite obduction, 78 continental rift, oceanic or continental subduction).

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80 2. Orthopyroxene & Raman: state of the art

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Pyroxenes are chain silicates of general formula M2M1Si₂O₆. In natural pyroxenes, the M2 and M1 sites are filled by Mg, Fe²⁺, Ca, Li, Mn, or Na and by Mg, Fe²⁺, Fe³⁺, Al, Cr, or Ti⁴⁺, Ti³⁺, Mn (and others) respectively; partial exchange of Al for Si is also possible (Tribaudino et al., 2017). Substitutions are made possible by the rather flexible structure that can accommodate cations with different ionic radii and charges, leading to a wide range of possible compositions (Cameron and Papike, 2018; Papike, 2018).

88 The chemistry of Mg-Fe-Ca pyroxenes is generally expressed by Mg# (especially for 89 orthopyroxenes, where calcium content is low) and by the percentages of the three end-member

90 compositions: enstatite (En, MgSiO₃), ferrosilite (Fe, FeSiO₃), and wollastonite (Wo, CaSiO₃). 91 Pyroxene crystallizes in monoclinic C2/c or orthorhombic *Pbca* structure. Orthorhombic pyroxene 92 has the M2 site filled almost completely by Mg and Fe, and the position of Raman peaks is affected 93 by the relative concentration of Mg, Fe, and Ca ions (Wang et al., 2001). In orthopyroxene, the 94 presence of 120 Raman peaks has been predicted, 20-30 of which can be observed in goodquality Raman spectra (Stalder et al., 2009; Stangarone et al., 2016). The small Mg²⁺ ion forms 95 short and strong chemical bonds, leading to higher wavenumber peak positions in the Raman 96 spectrum. Both Fe^{2+} and Ca^{2+} are larger than Mg^{2+} , and their presence shifts the peaks' locations to 97 98 lower frequencies (Huang, 2000). Numerous studies reported a very good linear correlation 99 between the position of Raman peaks and the Mg# of orthopyroxene (e.g., Mernagh & Hoatson, 100 1997; Huang et al., 2000; Tribaudino et al., 2012; Andò & Garzanti, 2014; Hu et al., 2015). The greater abundance of the larger Ca²⁺ ion mitigates the effect of the Fe/Mg substitution in the 101 clinopyroxene structure. As Ca and Fe^{2+} substitutions have similar effect, Mg# can thus be more 102 103 accurately determined by Raman spectroscopy in Ca-poor orthopyroxene (Tribaudino et al., 2011), 104 reaching excellent precision (3.0 and 0.4 weight% for natural and synthetic crystals, respectively; 105 Stalder et al., 2009). By combining the three major peaks of meteoritic and terrestrial 106 orthopyroxene, the Mg/(Mg+Fe+Ca) ratio was measured with an error of only 0.1% (Wang et al., 107 2001).

108 The most intense Raman peaks (vibration modes) in the pyroxene spectrum are connected to the 109 vibration of silicate chains bonds, which are unaffected by chemical or structural inhomogeneities (Wang et al., 2001). Most distinctive is the $v_3 + v_4$ (~655 and ~675 cm⁻¹, respectively) couplet, 110 which is related to the symmetrical bending of the Si-O_{bridging} bond (i.e., involving the oxygen 111 linking two tetrahedra), and $v_5 + v_6$ (~1002 and ~1020 cm⁻¹, respectively) couplet, related to the 112 113 stretching of the Si-O_{bridging} bond (Makreski et al., 2006; Stangarone et al., 2016). The $v_3 + v_4$ 114 couplet allows us to discriminate between orthopyroxene and clinopyroxene, the latter showing 115 only one strong narrow peak in this spectral region (with the exception of pigeonite; Tribaudino et 116 al., 2011). The v₃ and v₄ vibrational modes are both parallel to the c-axis, and thus independent of 117 crystal orientation (Wang et al., 2001). Instead, the v_5 and v_6 vibrational modes are strongly 118 dependent on crystal orientation.

- 119 Clusters of medium-intensity Raman peaks also occur in the 300-400 cm⁻¹ (M2–O octahedron
- 120 bending mode) and 510-570 cm⁻¹ (O–Si–O bending mode) wavenumber regions (White, 1975;
- 121 Mernagh & Hoatson, 1997; Huang et al., 2000). Peaks in the < 500 cm⁻¹ region are related to M1-O
- 122 and M2-O crystal-lattice stretching modes (Stangarone et al., 2016); most important to estimate
- 123 calcium content is the v_1 (~330 cm⁻¹) vibrational mode (Wang et al., 2001).

124 **3. Sample choice**

125

126 The choice of samples to be analysed represents the first step to investigate the compositional signatures apt to best discriminate among different types of source rocks in terms of both lithology 127 128 and geodynamic setting. In this study, we chose to focus on modern sands because a single 129 sediment sample contains a wide spectrum of detrital grains statistically representative of an entire 130 drainage basin, thus offering an efficiency gain relative to techniques focused on bedrock 131 (Greensfelder, 2002). In this way, we could take advantage of decades of quasi-worldwide modern-132 sand studies and of the collection of over 6000 catalogued sediment samples readily available at the 133 Laboratory for Provenance Studies (University of Milano-Bicocca).

To consider a complete range of lithologies generated and exposed in both orogenic and anorogenic settings, including obduction orogens, continental and arc crust, rift valleys, and continental or intraoceanic volcanic arcs, we selected 15 sand samples from very diverse key regions where source rocks containing significant amounts of orthopyroxene are exposed (Table 1). We thus included mantle harzburgites, lower crustal metagabbros, gabbronorites, and volcanic sequences ranging from andesite to trachyte and dacite, representing different tectono-stratigraphic levels within continental, arc, or oceanic lithosphere.

Structural level	Geodynamic setting	Geological domain	Main lithology	Location
		Hatay-Kiziildağ Complex	Harzburgite	Hatay Peninsula (Turkey)
MANTLE		Sema'il Complex	Harzburgite	Northern Oman Mountains
	CONTINENTAL	Ivrea-Verbano Mafic Complex	Granulitic gabbro	Southern Alps (Italy)
LOWER CR031	& ARC CRUST	Kohistan Arc	Metagabbro to granite	Northern Pakistan
		Andean Cordillera	Andesite and dacite	Río Desaguadero (Argentina)
	CONTINENTAL MAGMATIC	Andean Cordillera	Basalt to dacite	Río Grande (Argentina)
	ARC	Andean Cordillera	Basalt to dacite	Río Colorado (Argentina)
		Andean Cordillera	Dacite	Río Agrio (Argentina)
		Luzon island arc	Basalt to dacite	Taiwan Island
UPPER CRUST		Kamchatka island arc	Andesite	SE Kamchatcka (Russia)
		Lesser Antilles island arc	Andesite and dacite	Martinique Island
		South Aegean island arc	Andesite and dacite	Santorini Island (Greece)
		Mt. Amiata (Tuscan province)	Trachydacite	Orcia River (Italy)
		Elbrus Volcano	Andesite and dacite	Greater Caucasus (Russia)
	RIFT VALLEY	Virunga volcanic province	K-trachyte and latite	East African Rift (Rwanda)

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Table 1. Information on the 15 studied samples of orthopyroxene-rich river and beach sands exclusively or dominantly
 derived from a range of mantle, deep-crustal, and volcanic rocks generated in different geodynamic settings.

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145 3.1. Ophiolitic mantle

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147 To represent OPX-bearing mantle rocks we have chosen two sand samples, one derived from the

148 Hatay-Kizildağ Ophiolite Complex in southernmost Turkey and one from the Sema'il Ophiolitic

- 149 Complex in the Northern Oman Mountains.
- 150 The Hatay-Kizildağ Complex, a counterpart of the Troodos Complex of Cyprus, is a supra-

151 subduction-zone obducted ophiolite comprising serpentinized mantle rocks overlain by layered 152 gabbros, isotropic gabbros and diorites, sheeted dikes, island-arc tholeiites to boninites, and upper 153 Maastrichtian-Cenozoic cover strata. The 3-km-thick mantle harzburgites containing lenses of 154 dunite, wehrlite, lherzolite and feldspathic peridotite are cross-cut by gabbroic to doleritic dikes 155 (Dilek and Thy, 2009). The Kale beach in the Hatay Peninsula consists of lithic ultramaficlastic 156 sand containing mainly cellular serpentinite and subordinately serpentineschist grains, along with 157 gabbroic rock fragments. The extremely rich tHM (transparent-heavy-mineral) suite is dominated 158 by orthopyroxene associated with olivine (Garzanti et al., 2000).

The Sema'il Ophiolite, also generated in supra-subduction settings at a fast-spreading center around 95 Ma, consists of an 8–12 km-thick section of residual mantle harzburgites, overlain by a 5–8 kmthick crustal section including layered to foliated gabbros, hydrothermally altered diabase dikes, and pillow basalts capped by lower Cenomanian radiolarites (Lippard et al. 1986; Searle and Cox, 163 1999).

Lithic ultramaficlastic sand of Wadi Dayqat — draining the southern part of the Northern Oman Mountains where mantle rocks are extensively exposed — contains mostly cellular serpentinite and subordinate serpentineschist grains along with significant sedimentary detritus (mostly carbonate grains derived from cover strata), and minor gabbroic and metabasite rock fragments. The rich tHM suite is dominated by orthopyroxene associated with clinopyroxene, olivine, amphibole, and Crspinel (Garzanti et al., 2002a).

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171 3.2 Lower continental crust

To represent OPX-bearing gabbroic rocks of the lower continental crust we have chosen one sandsample derived from the Mafic Complex of the Ivrea-Verbano Zone in northern Italy.

175 The Ivrea-Verbano Zone, the deepest tectonic unit of the Southern Alps, comprises an up to 10 km-176 thick gabbroic body (Mafic Complex), intruded into high-grade metasediments at a crustal depth of 177 18–25 km during Early Permian times (Quick et al. 1994). The Mafic Complex includes ultramafic 178 cumulates and layered gabbros, followed by 5-7 km-thick gabbronorite grading upward to 179 monzogabbros and diorites (Rivalenti et al. 1981). Subsolidus re-equilibration under static 180 conditions gave rise to anhydrous assemblages including orthopyroxene, clinopyroxene, and garnet. 181 Retrograde growth of brown amphibole was confined to shear bands within the gabbros (Colombo 182 and Tunesi, 1999).

183 The plagioclase-dominated sand of the Strona di Postua River contains common gabbroic and a few 184 amphibolite and sillimanite-bearing rock fragments. The extremely rich tHM suite is dominated by 185 orthopyroxene associated with brown amphibole, garnet, and clinopyroxene (Garzanti et al., 2006;

- 186 Andò et al., 2014).
- 187

- 188 3.3. Arc crust
- 190 To represent OPX-bearing metamorphic and igneous rocks of deep-seated arc crust we have chosen191 one sand sample derived from the Kohistan Arc in northern Pakistan.

192 The Kohistan Batholith represents the dissected remnants of a magmatic arc fed by northward 193 subduction of Neotethyan oceanic lithosphere from Cretaceous to Paleocene times (Searle et al., 194 1999). The completely exposed 40–50 km-thick lithospheric section includes peridotites and 195 granulite-facies metagabbros at the base, amphibolite and greenschist-facies metasediments 196 intruded by layered gabbronorites, and the gabbroic to granitic rocks of the main calcalkaline 197 batholith overlain by a volcano-sedimentary succession (Jagoutz and Schmidt, 2012).

Plagioclase-rich quartzo-litho-feldspathic sand of the Swat River contains abundant metabasite (epidosite, amphibolite) grains with subordinate metapelite/metapsammite, mafic to felsic plutonic, and serpentinite rock fragments. The extremely rich tHM suite is dominated by blue-green hornblende associated with orthopyroxene, clinopyroxene, and epidote (Garzanti et al., 2005; Liang et al., 2019).

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204 3.4. Continental and island arcs

206 Two-thirds of the studied samples were selected to provide a relatively wide panorama of 207 subduction-related OPX-bearing volcanic source rocks. Testing areas include east-facing island arcs 208 (Kamchatka Peninsula in eastern Russia and Taiwan Island) and west-facing continental arcs (four 209 samples collected at different latitudes along the Andean Cordillera in Argentina) in the Pacific 210 domain, one east-facing island arc in the Atlantic domain (Martinique Island), one island arc and 211 one continental arc associated with north-eastward and westward subduction in the Mediterranean 212 domain (Santorini Island in Greece and Tuscan Province in Italy, respectively), and the highest 213 volcano in Eurasia (Mt. Elbrus in the Northern Caucasus Range of southern Russia).

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215 3.4.1. Andean cordillera

The Andean continental arc, generated by east-dipping subduction of Paleo-Pacific plates since Jurassic times, consists of N/S-trending belts of mostly granite/granodiorite intrusions and andesite lava flows (Kay et al., 2005). The southern Central Andes (Pampean segment) and northern Southern Andes (Payenia and northern Patagonia segments) exhibit significant along strike variation in subduction angle, degree of tectonic shortening, character and intensity of magmatism, and exposed geological units. The Pampean flat-slab segment between 27°S and 33°S is characterized by a ~ 600-km-long volcanic gap and comprises a Jurassic–Cenozoic magmatic arc (Cordillera Principal), Carboniferous–Triassic basement uplifts (Cordillera Frontal), a thin-skinned, fold-thrust belt (Precordillera), and the adjacent broken retroarc basin with basement-cored block uplifts (Sierras Pampeanas) (Ramos et al., 2002).

To the south, the Andes are characterized by the active Southern Volcanic Zone emplaced over exhumed Jurassic to Miocene magmatic rocks of the Cordillera Principal, with a thin-skinned belt locally involving basement, and a retroarc basin partitioned by broad and low-relief basement uplifts (Ramos and Kay, 2006). Plio-Quaternary calcalkaline lavas are mostly andesites and dacites, whereas the associated ignimbrites are mostly high-Si andesites, dacites and rhyolites. Orthopyroxene, more abundant than clinopyroxene in dacitic lavas, shows little compositional variation with lava differentiation (Mg# 85-70; Deruelle, 1982).

In the Payenia segment between 34°S and 37°S, extensive Quaternary basaltic fields constitute the largest retroarc mafic volcanic province on Earth (Ramos & Folguera, 2011). Widely distributed throughout the region and spanning from the Cordillera Principal to the retroarc basin are also Upper Carboniferous to Lower Triassic igneous rocks of the Choiyoi Group, including basalts and andesites in the lower part and rhyolitic lavas and ignimbrites in the upper part (Kleiman & Japas, 2009).

241 In modern sands derived from the eastern slopes of the central and southern Andes in Argentina, 242 orthopyroxene is observed to markedy increase southward from the Pampean flat-slab segment 243 drained by the Río Desaguadero, to the Payenia segment drained by the Río Colorado and its 244 headwater branch Río Grande, and to the northern Patagonia segment drained by the Río Agro 245 (Garzanti et al., 2021a, 2021b). The Río Desaguadero carries feldspatho-litho-quartzose sand with 246 felsic and subordinately intermediate and mafic volcanic grains derived from the Cordillera 247 Prinicpal and Frontal associated with sedimentary and metamorphic rock fragments derived from 248 the Precordillera and Sierras Pampeanas; the moderately poor tHM suite contains clinopyroxene, 249 orthopyroxene, and amphibole in subequal proportions. The Río Grande and Río Colorado carry 250 quartzo-feldspatho-lithic sand with mostly mafic and intermediate volcanic rock fragments and 251 minor sedimentary grains; the rich tHM suite mainly contains clinopyroxene associated with 252 orthopyroxene, brown hornblende and oxy-hornblende, and a few olivine grains. The Río Agro, a 253 branch of Río Negro, carries litho-feldspathic sand dominated by plagioclase displaying spectacular 254 oscillatory zoning associated with mafic and intermediate volcanic rock fragments; the rich tHM 255 suite mostly consists of orthopyroxene with subordinate clinopyroxene and very few olivine and 256 amphibole grains.

257 *3.4.2. Luzon arc*

The Luzon intraoceanic arc, fed by the eastward subduction of the Eurasian Plate beneath the Philippine Sea Plate, eventually collided with the Chinese continental margin in the late Miocene, thus starting the growth of the Taiwan doubly-vergent orogenic wedge (Byrne et al., 2011). Luzon Arc remnants are incorporated in the Coastal Range of eastern Taiwan Island, where middle to upper Miocene (15-5 Ma) low-K tholeiitic to medium-K calc-alkaline basaltic to dacitic lava flows and ignimbrites are exposed (Lai et al., 2017).

Feldspatho-lithic sand of the Gaoliao River, draining the western flank of the Chengkuang'ao Volcano, contains mafic and subordinately intermediate volcanic rock fragments, plagioclase, and a few shale/siltstone grains. The very rich tHM suite consists of clinopyroxene and orthopyroxene with a few brown amphibole grains (Garzanti and Resentini, 2016).

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270 *3.4.3. Kamchatka arc*

The Kamchatka arc lies above a long-lived subduction system. Active volcanoes are numerous in southern Kamchatka, where magmatism is generated by westward subduction of NW Pacific lithosphere beneath the Okhotsk Plate along the Kuril-Kamchatka Trench (Volynets et al., 2010). Among these, the Avachinsky Volcano is characterized by porphyritic basaltic andesite and low-K andesitic lavas and pyroclastic rocks (Viccaro et al., 2012).

Khalaktyrsky beach, situated near Petropavlosk south of the Avachinsky Volcano, consists of plagioclase-dominated feldspatho-lithic sand with mostly mafic and subordinate intermediate volcanic rock fragments. The extremely rich tHM suite consists mainly of orthopyroxene with clinopyroxene and a few olivine and brown amphibole grains (Garzanti and Andò, 2007).

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282 *3.4.4. Lesser Antilles arc*

284 The Lesser Antilles island chain is an intraoceanic volcanic arc generated by westward subduction 285 of the Atlantic Plate beneath the Caribbean Plate (Bouysse et al., 1990). Mont Pelée on Martinique 286 Island is a late Quaternary composite andesitic volcano largely made of pyroclastic deposits 287 produced by numerous Plinian, dome-forming, phreatomagmatic, and phreatic eruptions (Germa et 288 al., 2011). Most famous and deadliest was the 1902 eruption, when the city of Saint-Pierre was 289 destroyed by a *nuée ardente* resulting in ~30,000 casualties and very few survivors. Phenocrysts in 290 volcanic rocks are mainly plagioclase displaying oscillatory zoning, associated with olivine and 291 augitic clinopyroxene in basalts, with both clinopyroxene and orthopyroxene in andesites, and with 292 orthopyroxene in dacites (Dupuy et al., 1985).

293 Saint-Pierre beach, situated south of La Peleé Volcano, consists of plagioclase-dominated litho-

feldspathic sand with intermediate and mafic volcanic rock fragments. The extremely rich tHM
suite is orthopyroxene-dominated with clinopyroxene and a few brown amphibole grains (Limonta
et al., 2015).

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298 *3.4.5. South Aegean (Hellenic) arc*

The South Aegean volcanic arc is generated by north-eastward subduction of Ionian oceanic lithosphere beneath the extending Greek microplate (Agostini et al., 2010). The most active center is the Santorini island group, built on Mesozoic to Paleogene metapelites and marbles by several large explosive eruptions since ~2 Ma. The Akrotiri Volcanic Complex in the southern part of Thera (the main island) consists of upper Pleistocene (650-550 ka) andesitic to dacitic lavas and younger cinder cones (Druitt et al., 1999).

Red Beach on southern Thera is backed by a 60 m-high, up to 80°-dipping slope of red volcanic rocks subject to high rockfall hazard (Marinos et al., 2017). Its plagioclase-dominated feldspatholithic sand consists of mostly mafic and subordinate intermediate volcanic rock fragments. The very rich tHM suite contains clinopyroxene with subordinate orthopyroxene, minor olivine, and a few oxy-hornblende grains (Garzanti and Andò, 2007).

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312 *3.4.6. Tuscan magmatic provenance*313

Westward-subduction beneath the Apennines thrust-belt and opening of the Tyrrhenian back-arc basin triggered extensive late Cenozoic magmatism, with significant contribution of the downgoing Adriatic continental lithosphere to the felsic character of the Tuscan magmatic province (Serri et al. 1993). Mount Amiata in central Italy is a silicic volcano mainly consisting of trachydacitic lavas and pyroclastic products erupted at ~300 ka, followed by trachydacitic and latitic lavas and domes, with a terminal phase characterized by ultrapotassic olivine latite lavas (Ferrari et al., 1996).

The quartz-poor quartzo-lithic sand of the Orcia River, draining the Amiata volcano, mostly consists of carbonate and shale/siltstone rock fragments with only a few and mostly felsic volcanic grains and rare plagioclase. The moderately poor tHM suite is orthopyroxene-dominated with a few clinopyroxene grains (Garzanti et al., 2002b).

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325 *3.4.7. Greater Caucasus* 326

The Greater Caucasus marks the northernmost deformation front of the Arabia-Eurasia collision zone, where accelerated exhumation in the central part of the range has been associated with mantlesourced magmatism since the late Miocene (Vincent et al., 2020). In this region rises the late Quaternary Elbrus stratovolcano, characterized by mainly dacitic lavas and pyroclastic rocks 331 (Lebedev et al., 2010).

Feldspatho-lithic sand of the Baksan River, draining the southern flank of the Elbrus Volcano, contains intermediate to mafic volcanic grains with zoned plagioclase or pyroxene phenocrysts. Moderately rich tHM suites are orthopyroxene-dominated with oxy-hornblende and only a few clinopyroxene and zircon grains (Vezzoli et al., 2020).

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- 337 3.5. Continental rifts
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As a major difference with respect to subduction-related orogenic lavas, anorogenic volcanic rocks generally lack orthopyroxene. Exceptions however occur. To represent OPX-bearing lavas generated in continental-rift settings we have chosen one sand sample derived from the Virunga volcanic province in Rwanda.

343 In the western branch of the East African Rift, mainly potassic to ultrapotassic volcanism restricted 344 to accommodation zones between extensional basins initiated at 13-12 Ma and shows a northward 345 increase in alkaline character and CO₂ content (Ebinger and Furman 2003; Pouclet et al., 2016). 346 The Virunga district includes two active volcanoes in Congo and six extinct volcanoes and small 347 cones in Rwanda, where lavas largely erupted in the last 150 ka range from olivine-rich potassic 348 basanites to K-rich or Na-rich trachybasalts. Silica-saturated K-trachytes or latites with 349 orthopyroxene, less titaniferous clinopyroxene, and alkali-feldspar were erupted only from the early 350 Pleistocene Sabinyo Volcano (Rogers et al. 1998).

Feldspatho-lithic sand of the Muhe River, sourced from the Sabinyo Volcano, is dominated by mostly mafic volcanic rock fragments with abundant sanidine microliths set in a glassy groundmass associated with larger calcic plagioclase phenocrysts. The extremely rich tHM suite consists of clinopyroxene and subordinate orthopyroxene, olivine, and rare apatite and epidote (Garzanti et al., 2013).

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357 4. Methods

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359 4.1. Petrographic and heavy-mineral analyses

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A quartered fraction of each of the 15 selected sand samples was impregnated with epoxy resin, cut into a standard thin section, and analysed by counting ~400 points according to the Gazzi-Dickinson QFL method (Ingersoll et al. 1984). To collect full information on all rock fragment types and recalculate petrographic parameters according to both Gazzi-Dickinson QFL and traditional QFR methods we used a detailed point-counting sheet that allows the simultaneous registration of the mineral beneath the cross hair and of the rock fragment in which the mineral is 367 located (figure 5 in Garzanti, 2019). Sands were classified according to the proportions of the three 368 main groups of framework components (Q = quartz; F = feldspars; L = lithic fragments; 369 classification scheme after Garzanti, 2019). Median grain size was determined in thin section by 370 ranking and visual comparison with standards of $\phi/4$ classes prepared by sieving in our laboratory.

371 From a split aliquot of a conveniently wide size-window obtained by wet sieving (ranging from 63-372 250 µm to bulk sample for the best sorted sand), heavy minerals were separated by centrifuging in 373 Na-polytungstate (2.90 g/cm³) and recovered by partial freezing with liquid nitrogen (Andò, 2020). 374 In grain mounts, ≥ 200 transparent heavy minerals for each sample were either grain-counted by the 375 area method or point-counted at appropriate regular spacing to obtain correct volume percentages 376 (Garzanti and Andò 2019). Analyses were carried out by routinely coupling observations under the 377 optical microscope and the Raman spectroscope. Transparent heavy-mineral assemblages, called for 378 brevity "tHM suites" throughout the text, are defined as the spectrum of extrabasinal detrital 379 minerals with density >2.90 g/cm³ identifiable under a transmitted-light microscope. In the studied 380 samples, their concentration (tHMC) ranges from moderately poor to extremely rich (1-2% and > 381 20% of total extrabasinal detritus). Full information on samples and sampling sites, and the 382 complete petrographic and heavy-mineral datasets are provided in Appendix Tables A1, A2, and 383 A3, respectively.

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4.2. Optical and Raman spectroscopy analyses

For each of the 15 studied samples another split aliquot of the separated $> 2.90 \text{ g/cm}^3$ fraction was mounted on Huntsman Araldite® DBF resin and polished. On photographic maps of the mounts, each pyroxene grain was labelled by a progressive number. On each sample, a preliminary investigation on numerous orthopyroxene grains selected at random was carried out under a polarized Leica DM750 microscope, and the main optical features (i.e., colour, pleochroism, habit, z/c angle, birefringence, elongation, interference figures, optical sign) were recorded for 458 grains overall.

394 Taking care to avoid inclusions and weathering patinas, 500 Raman spectra overall were collected with a high-resolution Renishaw inViaTM equipped with a Leica DM2500 polarizing microscope 395 and motorized x-y stages, using a 50×LWD (long working distance) objective, a solid-state 532 nm 396 laser, and a grating of 1800 lines/mm in the 140–1900 cm⁻¹ range. Acquisition time was ~40 s, 397 space resolution < 5 μ m, spectral resolution \pm 0.5 cm⁻¹, and power \leq 10 mW at the sample. 398 399 Calibration was done before each experimental session with a silicon wafer standard (peak at 520.7 400 cm⁻¹). To expand the dataset and test its quality and reliability, 40 grains from different samples and 401 characterised by diverse Mg# were investigated at the University of Parma with a high-resolution 402 Horiba LabRam HR Evolution confocal micro-spectrometer (800 mm focal length) equipped with 403 an Olympus BX41 microscope and x-y-z motorized stage using a 100× objective, a He-Ne (632.8 404 nm) laser, and a 600 groves/mm blazed grating. Acquisition time was 50 s, space resolution ~1 μ m, 405 spectral resolution better than 0.5 cm⁻¹. Full widths at half maximum (FWHM) were measured on 406 these high-resolution spectra.

407 The software LABSPEC 5 (Horiba Ltd.) was used for baseline subtraction. Peak positions were 408 measured by the Gaussian–Lorentzian (pseudo-Voigt) deconvolution method, reaching an accuracy 409 of ± 0.3 cm⁻¹. The results of Raman analyses are provided in Appendix Tables A4 and A5.

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411 4.3. SEM-EDS minerochemistry

The 15 grain mounts were coated with graphite and over 600 analyses were made at the SEM-EDS (scanning electron microscopy-energy dispersive spectrometer), exactly on the same spot analysed by Raman spectroscopy, on 350 selected grains yielding higher, medium, and lower frequency Raman peaks reflecting higher, medium, and lower Mg content. By combining observations of the very same grains at the optical microscope, Raman spectroscope, and scanning electron microscope we could thus compare and confidently correlate optical properties, position of Raman peaks, and chemical compositions of 350 orthopyroxene grains.

420 Minerochemical analyses were carried out at the University of Milano-Bicocca with a TESCAN 421 VEGA TS Univac 5136 XM set with a EDAX GENESIS 4000 XMS Imaging 60 SEM electronic 422 microprobe, under an electron beam of 20-kV high voltage, 250-nm spot size, 45° take-off angle, 423 and current absorption 190±1 pA, measured in platinum Faraday cup. The quantification of main 424 elements (Mg, Fe, Ca, Na, Si, and Al) was calibrated with Astimex Scientific standards. 425 Compositions were calculated using PX-NOM software (Sturm, 2002) following the nomenclature 426 of Morimoto et al. (1988). The complete dataset of SEM-EDS analyses is provided in Appendix 427 Tables A6 and A7.

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437 **5. Results**

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439 5.1. Optical observations

MANTLE OPHIOLITE Kizildağ Complex	LOWER CRUST Ivrea-Verbano Zone	VOLCANIC ARC Elbrus Volcano	VOLCANIC ARC Martinique Island	VOLCANIC ARC Amiata Volcano
		and the second		

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Figure 2. Typical optical features displayed by orthopyroxene grains derived from mantle, lower crustal, and
volcanic rocks. Enstatite *s.s.* from the Kizildağ harzburgite is shown both at parallel and crossed polarizers,
whereas other orthopyroxenes are rotated by 90° to show their characteristic pleochroism. Scale bar: 100 μm.

- 444 Under the polarized microscope, virtually colourless and optically positive enstatite s.s., which 445 dominates the tHM assemblage of the two sands derived from the Kizildağ and Sama'il mantle 446 harzburgites where it commonly contains exsolution lamellae of clinopyroxene (Fig. 2), is readily 447 distinguished from pleochroic hypersthene s.l., which is dominant in all other samples. Pleochroism 448 intensity and colour vary depending on the observed crystal face: only the {100} face - most 449 commonly observed in grain mounts - shows strong pleochroism with yellow to pink versus green 450 shades, whereas the {010} face displays only greenish shades (Tröger, 1979; Mange and Maurer, 451 1992). Pleochroism is a complex phenomenon variously ascribed to: i) iron content and ordering; ii) 452 presence of Ti, Mn, Cr, Ni, or Al ions; iii) oriented inclusions and lamellae; iv) Al-driven lattice 453 distortion (Kuno, 1954; Burns, 1966).
- In this study, we failed to see a clear correlation between Mg# and pleochroism intensity, and noticed numerous Fe-rich orthopyroxene grains showing weak colour. Most evident is the difference in pleochroism between yellow-orange/green orthopyroxene derived from effusive volcanic rocks and pink-reddish/green orthopyroxene derived from deep-crustal Ivrea-Verbano and Kohistan intrusive rocks (Jan and Howie, 1980) (Fig. 2).
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461 5.2. SEM–EDS minerochemical data

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Geodynamic	11		SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	K₂O	Na₂O	Cr ₂ O ₃	Mg#	En	Fe	Wo
setting	Unit		wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	-	mol%	mol%	mol%
		Mean	56.6	b.d.l.	2.0	5.6	0.02	33.8	1.5	b.d.l.	b.d.l.	0.8	0.92	88.9	8.3	2.9
ш	Kiziildağ	Max	57.3	b.d.l.	2.5	5.9	0.2	34.5	2.3	b.d.l.	b.d.l.	1.0	0.96	89.9	8.7	4.2
UL N		Min	56.0	b.d.l.	1.6	5.2	b.d.l.	33.2	0.9	b.d.l.	b.d.l.	0.6	0.91	88.1	7.7	1.6
NAM		Mean	55.4	0.3	2.2	6.8	0.3	32.2	1.2	0.1	0.3	1.1	0.91	87.0	10.7	2.3
Р.	Sema'il	Max	56.6	0.4	3.3	8.8	0.4	33.3	2.1	0.3	0.4	1.4	0.94	88.4	13.9	4.1
		Min	54.3	0.2	0.8	5.8	0.2	31.6	0.6	b.d.l.	0.08	0.7	0.87	84.9	9.3	1.1
ST	luraa Varbana	Mean	52.0	0.02	2.4	21.4	0.0	22.2	0.5	b.a.i.	0.02	b.d.l.	0.05	72.0	35.5	1.1
RU RU	Iviea-verballo	Min	51 3	0.2 hdl	1.6	16.3	0.0	17.6	0.0	b.u.i. h.d.l	b.d.l	b.d.i.	0.73	72.9 51 Q	26.1	0.0
		Mean	51.5	b.d.l.	1.7	24.3	0.5	20.4	0.8	b.d.l.	b.d.l.	b.d.l.	0.61	58.5	40.0	1.6
AR(Kohistan	Max	52.7	b.d.l.	2.2	25.9	0.8	21.4	1.1	b.d.l.	b.d.l.	b.d.l.	0.63	60.7	43.3	2.4
C ≪	rternetari	Min	50.9	b.d.l.	1.0	23.1	0.3	18.7	0.4	b.d.l.	b.d.l.	b.d.l.	0.57	54.3	37.6	0.7
	Pío	Mean	53.9	0.6	1.2	18.0	0.3	24.5	1.6	0.2	0.3	0.02	0.73	68.3	28.5	3.2
0	Desaguadero	Max	56.2	0.8	2.7	21.1	0.5	30.8	2.0	0.4	0.5	0.5	0.88	82.9	33.7	4.2
4R((Argentina)	Min	523	03	05	97	01	22.2	10	0.06	01	hdl	0.66	63.5	14.8	20
IC		IVIIII	54.7	0.0	0.0	17.1	0.1	22.2	1.5	0.00	0.1	b.d.l.	0.00	66.7	30.2	2.0
ЛАТ	Río Grande	Mean	54.7	0.5	0.5	04.4	0.4	25.2	1.5	0.2	0.4	b.u.i.	0.03	74.7	30.2	2.0
JGN	(Argentina)	Max	55.8	0.7	1.0	21.4	0.6	25.5	1.9	0.3	0.8	D.d.I.	0.74	/1./	35.4	3.9
W		Min	53.5	0.3	0.2	15.7	0.2	21.1	1.0	0.1	0.2	D.a.I.	0.64	67.3	25.2	2.2
TAL	Río Colorado	Mean	53.9	0.2	0.7	18.6	0.9	24.1	1.6	b.d.l.	0.3	0.02	0.71	66.7	30.3	3.1
EN	(Argentina)	Max	55.1	0.4	1.3	22.0	1.7	26.3	2.4	b.d.l.	0.6	0.3	0.80	71.3	35.6	4.8
NIT.	,	Min	53.1	0.1	0.5	15.4	0.5	21.5	1.1	b.d.l.	0.2	b.d.l.	0.65	61.4	24.3	2.2
NO	Río Agrio	Mean	53.0	0.4	0.7	24.8	0.6	18.8	1.5	b.d.l.	0.3	b.d.l.	0.58	55.1	41.7	3.2
O	(Argentina)	Max	54.9	0.7	2.4	27.0	1.1	24.8	2.0	b.d.l.	0.8	b.d.l.	0.74	71.2	44.2	4.2
	(3)	Min	50.7	0.2	0.3	15.3	0.3	17.5	1.3	b.d.l.	0.05	b.d.l.	0.55	52.9	25.1	2.5
		Mean	53.2	0.4	1.2	18.2	0.5	24.8	1.5	0.1	0.2	0.3	0.73	68.2	28.9	2.9
	Taiwan	Max	54.2	0.5	1.7	20.1	0.7	27.5	2.0	0.2	0.4	0.5	0.83	74.9	31.7	3.8
		Min	52.0	0.2	0.7	13.4	b.d.l.	23.6	0.8	b.d.l.	0.09	b.d.l.	0.70	65.4	21.2	1.6
		Mean	52.5	0.4	1.4	17.9	0.4	25.0	1.6	0.2	0.2	0.09	0.75	68.7	28.2	3.1
	Kamchatka	Max	53.5	0.6	2.4	21.1	0.7	26.3	2.0	0.3	0.4	0.2	0.80	71.7	34.2	4.0
		Min	51 5	0.3	0.6	159	02	22.7	10	0.04	01	hdl	0.68	63.5	24.6	21
		Meen	50.5	0.0	0.0	26.1	12	19.4	1.0	hdl	0.2	0.3	0.60	54.2	43.0	2.8
RC	Mortiniquo	wean	53.4	0.7	1.9	20.1	1.5	21.0	1.4	b.d.i.	0.4	0.5	0.60	50.2	49.0	2.0
CAL	iviartiriique	Мах	40.4	0.7	0.0	29.4	1.5	47.0	0.0	b.u.i.	0.4 6 d l	0.5	0.03	40.0	40.1	17
NNA		Min	40.4	0.2	0.3	23.5	0.8	17.5	0.9	0.0.1.	D.u.i.	0.1	0.55	49.2	37.7	1.7
rc/		Mean	51.0	0.4	0.8	22.7	0.9	22.4	1.6	0.1	0.2	0.01	0.66	59.9	36.9	3.2
VO	Santorini	Max	53.6	0.6	1.3	26.7	1.4	43.5	2.2	0.2	0.3	0.07	0.72	66.4	44.9	4.4
		Min	50.7	0.3	b.d.l.	16.1	0.3	18.2	0.4	0.05	b.d.l.	b.d.l.	0.58	52.1	19.2	0.5
		Mean	49.8	0.4	0.6	32.0	0.4	14.7	1.5	0.2	0.1	b.d.l.	0.47	43.3	53.6	3.1
	Amiata	Max	51.5	0.7	1.4	35.0	0.7	17.0	1.8	0.4	0.4	b.d.l.	0.54	49.3	57.9	3.7
		Min	48.5	b.d.l.	b.d.l.	28.6	0.2	13.2	1.1	b.d.l.	b.d.l.	b.d.l.	0.41	38.9	47.3	2.4
		Mean	54.2	0.4	1.3	17.2	0.5	25.7	1.3	b.d.l.	b.d.l.	0.2	0.73	70.2	27.3	2.5
	Elbrus	Max	55.1	0.4	2.6	21.7	0.8	29.0	1.6	b.d.l.	b.d.l.	0.5	0.81	77.7	34.9	3.1
		Min	52.8	0.2	0.5	12.5	0.3	22.9	1.0	b.d.l.	b.d.l.	b.d.l.	0.65	63.3	19.2	1.9
_ ` _		Mean	52.1	0.5	0.9	22.3	0.2	20.9	1.6	b.d.l.	0.2	0.2	0.63	60.2	36.4	3.4
	Virunga	Max	52.9	0.5	1.1	25.6	0.3	22.8	1.8	b.d.l.	0.3	0.3	0.69	64.8	42.1	3.6
ÅЯ	-	Min	51.4	0.4	0.5	19.7	0.2	18.7	1.5	b.d.l.	0.2	b.d.l.	0.57	54.6	31.8	3.2

463

464 Table 2. Chemical composition of detrital othopyroxenes analyzed by SEM-EDS. Note high Si and Cr in 465 Mg-rich OPX from mantle rocks and low Ca in OPX from lower-crustal Ivrea-Verbano metagabbros and 466 Kohistan arc intrusives; all these OPX are Ti-poor. Fe-rich OPX from Mt. Amiata is poor in Si and Al. No 467 distinctive features are displayed by OPX from Virunga trachytes. Mg#: Mg/(Mg+Fe) atomic ratio; En: 468 enstatite; Fs: ferrosilite; Wo: wollastonite; b.d.l.: below detection limit.

469 As anticipated (e.g., Dilek & Newcomb, 2003), detrital orthopyroxene from mantle rocks yielded

470 much higher Cr $(0.9\pm0.2 \text{ wt\% Cr}_2O_3)$ and Mg concentrations (Mg# 0.92 ± 0.02 ; En 88 ± 1) than all

471 other samples (Cr₂O₃ \leq 0.5 wt%; Mg# 0.67±0.07; En 63±7). SiO₂ is also high, whereas TiO₂ is low

472 (Table 2). Mg# is highest in Kizildağ-derived sand and Cr highest in the Sama'il-derived sand (Fig.

473 <mark>3</mark>).



Figure 3. Chemical composition of detrital othopyroxenes determined by SEM-EDS. The 350 analyzed
grains from 15 sand samples provide a statistical representation of a range of source-rock lithologies at
different structural levels of continental crust, arc crust, and oceanic lithosphere. Only a few grains yielded
En values between 85 and 75. En: enstatite; Fs: ferrosilite; Wo: wollastonite. Colour codes similar as in Fig.
6.

Detrital orthopyroxenes from lower-crustal Ivrea-Verbano granulitic metagabbros and Kohistan intrusive rocks are singled out by their calcium content, notably lower (Wo $1.3\pm0.4\%$) than both mantle-derived (Wo 2.4 ± 0.9) and volcanic-derived orthopyroxene (Wo $3.1\pm0.6\%$). It must be noted, however, that Ca determination by SEM-EDS may be influenced by the presence of clinopyroxene or plagioclase impurities (Lindh, 1975). Ivrea-Verbano orthopyroxenes show two populations (Mg# 73-71 and 64-52), whereas Kohistan orthopyroxenes are tightly clustered (Mg# 0.61 ± 0.2) (Fig. 3). TiO₂ is also low (Table 2).

487 Detrital orthopyroxene in the 10 studied sands derived from intraoceanic to continental volcanic 488 arcs yielded compositions ranging widely from Mg# 80 to Mg# 40, broadly showing three clusters. 489 The main cluster centered at Mg# 70 comprises orthopyroxene grains derived from andesites of the 490 Andean Cordillera and carried by the Desaguadero, Grande, and Colorado Rivers. Slightly richer in 491 Mg are orthopyroxenes from the Luzon Arc in Taiwan, Elbrus Volcano in the Greater Caucasus, 492 and Avachinsky Volcano in Kamchatka, and the few richest Mg-rich grains (Mg# 80-75) were 493 found in Desaguadero, Colorado, Elbrus, Kamchatcka, and Taiwan sands (Fig. 3). A second main

- cluster centered at Mg# 55 comprises orthopyroxene grains derived from dacites of the Andean
 Cordillera and carried by the Agrio River or found in the Saint Pierre beach on Martinique Island.
 Both of these two main clusters are represented in the Red beach on Santorini Island (Fig. 3). A
 third cluster (Mg# 50-40) is defined by the Fe-rich orthopyroxene grains shed by the trachydacites
 of the Amiata Volcano in Tuscany, which are poor in SiO₂ and Al₂O₃ (Table 2).
- 499 Detrital orthopyroxene from the rift-related Virunga trachytes (Mg# 0.62 ± 0.03 ; En 60 ± 3) can 500 hardly be distinguished from grains shed by volcanic arcs, although they tend to have slightly more 501 Ca (Wo 3.5 ± 0.3) (Fig. 3).
- 502 According to the traditional classification (Poldervaart, 1947), orthopyroxene grains from the 503 Kizildağ harzburgites (En 90-88) will all classify as enstatite, whereas some grains from Sema'il 504 harzburgites (En 88-85) turned out to be magnesium-rich bronzites despite their very similar optical 505 properties (Fig. 2). Iron-rich bronzites (Mg# 0.8-0.7) are the most common orthopyroxene in 506 Kamchatka, Elbrus and Taiwan sands and are as common as magnesium-rich hypersthene (Mg# 507 0.7-0.6) in most Andean samples (Desaguadero, Grande, and Colorado Rivers). Hypersthene is 508 prevalent in Ivrea-Verbano sand derived from lower crustal metagabbros and dominant in Kohistan 509 sand derived from arc intrusives as in Virunga sand derived from rift-related trachytes. Hypersthene 510 with bimodal composition (Mg# 0.7-0.65 and 0.6-0.55) characterizes Santorini beach sand. Low-511 magnesium hypersthene (Mg# 0.6-0.55) dominates Agrio sand from dacites of the Andean 512 Cordillera. Fe-hypersthene is found and dominant only in sand from the silicic Amiata Volcano.
- 513 SEM-EDS analyses also highlighted the relationships among the concentrations of diverse chemical
- elements in orthopyroxene. This issue was investigated by Howie and Smith (1966), who found that
- 515 Mg# correlates well with Cr, Ni and Al, anticorrelates with Ca and Mn, and is uncorrelated with Ti.
- 516 In the 350 analysed detrital orthopyroxenes, Mg# correlates positively with SiO₂ (r 0.70), Al₂O₃ (r
- 517 0.58), and Cr_2O_3 (r 0.62), whereas no correlation was observed with CaO (Fig. 4). TiO₂ correlates
- 518 with CaO (r 0.60), K₂O (r 0.44), and Na₂O (r 0.37). MnO correlates weakly positively with FeO (r
- 519 0.33) and negatively with all other elements. Al₂O₃ correlates weakly negatively with CaO (r 0.38).



520

521 Figure 4. Relationships among major chemical elements hosted in detrital orthopyroxenes as determined by 522 SEM-EDS. OPX from mantle harzburgites is highest in Mg, OPX from lower continental and arc crust 523 poorest in Ca. Volcanic OPX, poorer in Al, displays decreasing Mg# from andesite to dacite and more felsic 524 source rocks. Arc and rift-related volcanic OPX are not different. The biplot (Gabriel, 1971) drawn using 525 CoDaPack software by Comas-Cufí and Thió-Henestrosa, 2011) displays multivariate observations (points) 526 and variables (rays). The length of each ray is proportional to the variance of each element in the dataset. If 527 the angle between two rays is close to 0°, 90°, and 180°, then the corresponding compositional parameters 528 are directly correlated, uncorrelated, and inversely correlated, respectively. Colour codes similar as in Fig. 6.

6. Raman spectroscopy analysis of orthopyroxene

A main goal of this study was to provide a robust time-saving method to estimate Mg# and thus
distinguish among several orthopyroxene compositions during routine provenance analysis. About
500 Raman spectra were collected, 350 of which were related to the chemical composition.

After baseline subtraction and deconvolution (Fig. 5), all peak positions were reported in ExcelTM sheets. The 300-400 cm⁻¹ cluster was considered as the sum of four vibrational modes (v_1 and v_2 being those with the lowest and highest frequencies). The six most intense and clearly distinguishable peaks were considered for Mg# estimation (Table 3): v_1 (~ 330 cm⁻¹); v_2 (~ 395 cm⁻ v_3 (~ 655 cm⁻¹); v_4 (~ 675 cm⁻¹); v_5 (~ 1002 cm⁻¹); and v_6 (~ 1020 cm⁻¹). Plots in Fig. 6 permit an

- 539 accurate correlation among vibrational modes and Mg content in orthopyroxene, thus allowing a
- 540 ready estimate of Mg# during routine provenance analysis.
- 541

Geodynamic	11 14			v ₁	V ₂	V ₃	V 4	V 5	V ₆
setting	Unit	Mg#		cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹
		0.92	Mean	343.4	400.8	662.1	683.8	1011.5	1030.1
잍	Kiziildağ	0.96	Max	344.3	402.3	662.7	684.6	1012.9	1031.0
		0.91	Min	342.1	398.5	661.4	683	1010.1	1028.4
HIC		0.91	Mean	343.5	400.5	661.9	683.9	1010.3	1030.5
	Sema'il	0.94	Max	345.0	403.8	662.8	684.9	1012.6	1033.1
_		0.87	Min	341.2	397.8	661.2	683.3	1009.7	1027.1
ТГ		0.65	Mean	335.9	393.6	654.8	675.6	1000.1	1014.6
US [.]	Ivrea-Verbano	0.75	Max	340.8	402.1	658.0	679.4	1004.2	1022.1
CRI		0.53	Min	332.5	384.2	652.4	672.1	996.7	1007.0
L D		0.61	Mean	334.7	389.8	654.6	674.3	999.3	1013.6
AF	Kohistan	0.63	Max	336.7	399.2	656.2	676.0	1001.0	1021.1
0 %		0.57	Min	332.2	382.0	652.7	672.5	997.6	1009.4
	Río	0.73	Mean	333.7	394.4	656.1	675.8	1003.8	1021.9
I RC	Desaguadero	0.88	Max	340.9	401.1	660.0	681.6	1007.8	1030.5
C♭	(Argentina)	0.66	Min	331.0	387.3	654.1	673.5	1001.5	1016.8
АТІ	Día Cranda	0.69	Mean	331.8	393.0	655.3	674.6	1002.9	1019.9
M U	(Argentina)	0.74	Max	335.7	397.4	657.4	676.6	1005.2	1024.4
MAG	(/ ingentina)	0.64	Min	326.6	387.9	652.8	672.0	1000.3	1016.3
AL I	Día Calarada	0.71	Mean	332.9	394.5	655.9	675.3	1003.1	1018.2
ÎN.	(Argentina)	0.80	Max	335.1	403.4	657.7	677.2	1005.0	1022.9
Щ	(, ingoniana)	0.65	Min	330.5	390.0	654.3	673.3	1001.2	1012.8
ITN	Pío Agrio	0.58	Mean	329.6	390.2	653.3	672.5	1000.9	1015.1
100	(Argentina)	0.74	Max	336.4	397.6	656.8	677.5	1005.2	1023.4
0	(,	0.55	Min	328.4	386.8	652.6	671.6	999.8	1010.4
		0.73	Mean	333.8	395.0	656.4	676.2	1003.6	1019.7
	Taiwan	0.83	Max	336.2	399.5	658.2	678.1	1006.5	1024.9
		0.70	Min	326.4	392.4	655.5	675.1	1002.3	1011.0
		0.75	Mean	333.5	393.8	656.0	675.7	1003.6	1021.9
	Kamchatka	0.80	Max	336.3	398.0	657.4	677.4	1005.9	1026.3
		0.68	Min	329.0	389.3	653.0	673.2	1001.4	1016.4
о С		0.61	Mean	329.9	390.5	653.6	672.3	1000.0	1014.9
AF	Martinique	0.69	Max	332.8	397.4	655.1	674.0	1001.7	1019.8
NIC		0.53	Min	328.0	385.7	652.0	670.9	998.3	1011.8
CA		0.66	Mean	330.8	392.1	654.2	673.4	1001.8	1018.4
OL	Santorini	1.00	Max	334.2	402.4	660.8	676.6	1006.7	1022.8
>		0.58	Min	327.9	386.9	651.4	670.8	999.7	1013.8
		0.47	Mean	324.9	384.8	650.0	668.7	996.6	1010.4
	Amiata	0.54	Max	328.3	395.3	651.7	670.2	997.5	1016.9
		0.41	Min	322.1	377.1	648.9	667.5	995.8	1001.4
		0.73	Mean	333.5	395.7	655.9	675.8	1002.6	1019.5
	Elbrus	0.81	Max	339.1	400.9	659.3	680.0	1006.5	1024.9
		0.65	Min	326.7	387.7	652.6	671.9	999.7	1008.2
Ŀ Ч		0.63	Mean	331.1	390.8	654.1	673.1	1000.9	1016.7
ALL ALL	Virunga	0.69	Max	332.5	395.7	655.6	674.6	1004.5	1021.6
_≯		0.57	Min	328.9	386.8	652.5	671.7	999.2	1012.6

543 Table 3. Mean, minimum and maximum Raman peak positions (vibrational modes v1 to v6) distinctive of
544 detrital othopyroxene derived from a range of mantle, deep crustal, and volcanic rocks representing different
545 geodynamic settings. Mg#: Mg/(Mg+Fe) atomic ratio.





547 Figure 5. Selected Raman spectra of orthopyroxene grains from diverse source rocks in different 548 geodynamic settings. Baseline subtraction was obtained with Labspec 5 software. Greater background noise 549 for Cr-rich harzburgite-derived OPX is ascribed to Cr-induced fluorescence (Savel'eva et al., 2013). Peaks 550 are stronger for more ordered OPX derived from lower-crustal granulitic metagabbro. In the low-wavelength 551 spectral region, peaks' shape and relative intensity depends on crystal orientation.

As previously documented (e.g., Wang et al., 2001; Stalder et al., 2009), Raman peak positions are linearly correlated to Mg content (right panels in Fig. 6) and one to the other (selected peak combinations are shown in left panels of Fig. 6). Six formulas to calculate Mg content from peak frequencies were thus obtained (Table 4).

Vibrational modes	Equations (cm ⁻¹)	R ²	σMg#
v₁ (~ 330 cm ⁻¹)	Mg# = (v ₁ - 309.0) / 34.9	0.8	0.19
v ₂ (~ 395 cm ⁻¹)	Mg# = (v ₂ - 372.0) / 31.3	0.52	0.31
v ₃ (~ 655 cm⁻¹)	Mg# = $(v_3 - 639.5) / 23.2$	0.88	0.15
v₄ (~ 675 cm⁻¹)	Mg# = (v ₄ – 655.1) / 29.2	0,88	0.13
v ₅ (~ 1002 cm ⁻¹)	Mg# = (v ₅ – 984.5) / 26.5	0.85	0.16
v ₆ (~ 1020 cm ⁻¹)	Mg# = (v ₆ - 989.9) / 42.4	0.72	0.21

556

557**Table 4.** Mg# calculated from Raman peak positions. R^2 and σ Mg# represent the proportion of the variation558and expected uncertainty when Mg# is derived from the value of a single Raman peak.





Figure 6. Sensitivity of Raman peak positions to Mg# in detrital orthopyroxene as determined by SEM-EDS. The best correlation between peak position and Mg# is obtained for vibrational modes v3 and v4, which display excellent linear correlation with each other (middle panel to the right). Among other peaks, v_1 , v_5 , and v_6 can be used to increase the accuracy of Mg# determination, whereas v_2 is least reliable. Colour scale reflects decreasing Mg# from red (Mg# 1.0) to blue (Mg# 0.4).

565 The correlation is strongests for v_1 , v_3 , v_4 , and v_5 and weaker for v_2 and v_6 , largely because of their 566 lower intensity and consequent difficulty in the deconvolution and precise assessment of peak frequencies. The intense narrow couplet around 660 cm⁻¹ thus allowing a very accurate measure of 567 568 both band positions is the most reliable for Mg# estimation. A good correlation between Mg content 569 and peak locations is also hampered by the variable amount of calcium, which in the studied grains 570 is lower in continental and arc crust orthopyroxenes (Ivrea Verbano and Kohistan) than in the other 571 samples. For this reason, Huang et al. (2000) proposed two different formulas for Ca-rich and Ca-572 poor orthopyroxene, obtaining a lower error. Calcium content, however, must be known 573 beforehand. Because v_1 correlates negatively with calcium content (Tribaudino et al., 2012; 574 Stangarone et al., 2016), Ca-poor Ivrea Verbano and Kohistan orthopyroxenes plot above the 575 wavenumber/Mg# regression line for the v_1 (~ 330 cm⁻¹) peak, resulting in higher frequencies for 576 the same Mg/Fe ratio. Among other peaks, only v_5 is slightly sensitive to calcium content. No 577 correlation with Al content was found.

578 Full widths at half maximum (FWHM) for all six vibrational modes were measured to test the 579 potential of Raman analysis to distinguish between volcanic and highly ordered metamorphic 580 orthopyroxenes (Ghose and Hafner, 1967). No significant difference, however, was observed 581 among orthopyroxene shed by mantle ophiolites, lower crustal metagabbros, and volcanic rocks.

582

583 **7. Provenance implications**

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This study was aimed at testing whether orthopyroxene grains derived from a range of source-rock lithologies belonging to different tectono-stratigraphic levels and generated in different geodynamic settings have sufficiently distinct chemical composition to be distinguished by Raman spectroscopy during provenance analysis.

589 Several previous studies were dedicated to discriminate orthopyroxene hosted in intrusive versus 590 metamorphic rocks. Bhattacharyya (1971) suggested that metamorphic orthopyroxene has higher 591 MgO+FeO+Fe₂O₃ because of replacement of Mg²⁺ by heavier Fe²⁺, as well as higher Al₂O₃ because 592 of higher pressure conditions. Rietmeijer (1983) broadly confirmed the tendency of metamorphic 593 orthopyroxene to have higher MgO+FeO+Fe₂O₃ but considered that Al₂O₃ rather tends to 594 principally reflect the whole-rock chemistry and coexisting or co-precipitating phases. He observed 595 further that metamorphic orthopyroxene has typically low Wo (Deer et al., 1978), and that igneous 596 orthopyroxene may shift into the field of lower-Ca metamorphic orthopyroxene during re-597 equilibration at high-grade metamorphic conditions. Fewer studies were dedicated to volcanic

598 orthopyroxenes, which were found to contain more significant Fe^{3+} (Ghose and Hafner, 1967; Deer 599 et al., 1978).

600 Our dataset is largely consistent with such previously acquired knowledge. Colourless and optically 601 positive orthopyroxene shed by ultramafic mantle rocks was confirmed to be the richest by far in 602 Mg and Cr. Orthopyroxene derived from gabbroic rocks re-equilibrated at high-grade metamorphic 603 conditions in the deep structural levels of continental (Ivrea-Verbano) or arc crust (Kohistan), 604 optically distinguished by their pink/green pleochroism, resulted to be poorest in Ca. Volcanic 605 orthopyroxene, optically distinguished by yellow-orange/green pleochroism, resulted to be 606 commonly richer in Fe³⁺, especially in Kamchatka, Taiwan and Santorini sands but less so in sands 607 derived from the Andean Cordillera or Elbrus and Virunga volcanoes.

608



609

610 Figure 7. Provenance determination of detrital orthopyroxene with Raman spectroscopy. The 3D plot 611 discriminates OPX composition by using the narrow v_3 peak (correlating best with Mg#) together with v_1

612 (useful to assess Ca content) and the strong v_5 peak. Colour codes similar as in Fig. 6.

613 Raman spectroscopy analyses (Fig. 7) allowed us to clearly distinguish among Mg-rich orthopyroxene from mantle harzburgites ($v_1 > 342$ cm⁻¹; $v_3 > 661$ cm⁻¹; $v_5 > 1009$ cm⁻¹), Ca-poor 614 615 orthopyroxene from gabbroic rocks re-equilibrated at high-temperature conditions in the lower 616 continental or arc crust (high $v_1/Mg\#$ ratio), and orthopyroxene from mafic to felsic volcanic rocks. Volcanic orthopyroxenes characterized by progressively lower Mg# are distinguished by an up to 617 618 20 cm⁻¹ shift of all Raman peaks towards lower frequencies. Grains from trachydacites (best fit: v₁: 619 322-328; v₃: 649-652; v₅: 995-998), dacites (best fit: v₁: 328-333; v₃: 653-655; v₅:999-1003), and 620 andesites (best fit: v1: 332-339; v3: 653-657; v5: 1002-1007) could thus be discriminated (Fig.7). 621 Raman analysis could not distinguish between orthopyroxene from rift-related and arc-related lavas. 622 In summary, optical observations alone are sufficient to discriminate colourless and optically 623 positive enstatite s.s. shed by mantle rocks from optically negative pleochroic hypersthene s.l., with 624 the possibility to distinguish further between intrusive/metamorphic and volcanic grains based on 625 their pink/green versus yellow-orange/green pleochroism (Fig. 2). The precise reliable identification 626 of several different provenances, however, requires coupling of optical observations with either 627 chemical or Raman analyses: 1) Mg-rich enstatite s.s. from mantle ophiolites; 2) Ca-poor 628 hypersthene s.l. from crustal gabbroic rocks; 3) hypersthene s.l. from volcanic rocks, with Mg# 629 decreasing from andesites (3A; Mg# 70-65) to dacites (3B; Mg# 60-50), and felsic differentiates 630 (3C; Mg# 50-40). Orthopyroxene derived from rift-related lavas may be characterized by a slightly 631 higher Ca content.

632

633 8. Conclusions

634

635 Coupling optical observations, SEM-EDS minerochemical analyses, and Raman spectra obtained 636 on 350 orthopyroxene (OPX) grains from 15 modern river and beach sands representing different 637 tectono-stratigraphic levels of continental, arc, and oceanic lithosphere in different geodynamic 638 settings allowed us to distinguish among three main provenances: 1) colourless and optically 639 positive Mg-rich and Cr-rich OPX derived from mantle harzburgites; 2) optically negative Ca-poor 640 OPX showing characteristic pink-reddish/green pleochroism derived from gabbroic rocks re-641 equilibrated at high temperature conditions in the lower continental crust or arc crust; 3) optically 642 negative OPX showing yellow-orange/green pleochroism derived from volcanic rocks and 643 identified by Mg/(Mg+Fe) atomic ratio decreasing progressively from andesite to dacite and more 644 felsic differentiates. Apart from slightly higher Ca content, OPX from rift-related lavas cannot be 645 distinguished from OPX in volcanic arcs. Chemical data allowed to differentiate among bronzite 646 and hypersthene, which could not be done with optical observations alone.

Accurate information on the chemical composition of detrital orthopyroxene can be very efficiently obtained by Raman spectroscopy, allowing us to build a large and thus more statistically representative database. Although chemical information can be only indirectly obtained, by this simple-to-perform technique we can, in a few seconds and with no additional sample preparation, successfully identify and characterize grains down to the size of a few microns. Changes in En, Fe and Wo in the crystal lattice can be effectively detected by measuring the position of only a few intense Raman vibrational modes.

The present study shows how orthopyroxene contained in mantle rocks exposed in obducted ophiolitic complexes, derived from deep crustal rocks, and shed from volcanic products with different silica content can be most readily distinguished by measuring the positions of the main characteristic Raman peaks (especially $v_1 \sim 330$ cm⁻¹, $v_3 \sim 655$ cm⁻¹ or $v_4 \sim 675$ cm⁻¹, and $v_5 \sim 1002$ cm⁻¹). Raman spectroscopy is thus proved to represent a powerful means to efficiently obtain robust high-resolution information in provenance studies.

660

661 ACKNOWLEDGMENTS

The studied samples, partly provided by Piero Bellotti, Silvia Bragherio, Giacomo Ghielmi, Filippo Lazzati, Giuditta Radeff and Annalisa Tunesi, were analysed by Giovanni Vezzoli, Alberto Resentini and Ferdinando Moretti Foggia for framework petrography, and by Sergio Andò, Mara Limonta and Marta Padoan for heavy minerals. Mineralogical insights offered by Maria Luce Frezzotti and Rosario Esposito, and technical help by Giovanni Coletti and Guido Pastore are also heartedly acknowledged. The manuscript benefited from careful handling and constructive advice by Editor ... and Reviewers ...

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671 SUPPLEMENTARY MATERIAL

572 Supplementary materials associated with this article include information on samples and sampling 573 sites (Table A1), the sand petrography (Table A2) and heavy-mineral datasets (Table A3), the 574 results of Raman spectroscopy analyses carried out at the laboratories of Milano (Table A4) and 575 Parma (Table A5), and the results of SEM-EDS minerochemical analyses (summarized in Table A6 576 and provided in full in Table A7).

677

678 FIGURE CAPTIONS

- Figure 2. Comparison between traditional (upper panel; Poldervaart and Hess, 1947) and IMA
 (lower panel; Morimoto et al., 1988) orthopyroxene classification schemes. En: enstatite; Fs:
 ferrosilite; Wo: wollastonite.
- 682

Figure 2. Typical optical features displayed by orthopyroxene grains derived from mantle, lower crustal, and volcanic rocks. Enstatite *s.s.* from the Kizildağ harzburgite is shown both at parallel and crossed polarizers, whereas other orthopyroxenes are rotated by 90° to show their characteristic pleochroism. Scale bar: $100 \mu m$.

- Figure 3. Chemical composition of detrital othopyroxenes determined by SEM-EDS. The 350
 analyzed grains from 15 sand samples provide a statistical representation of a range of source-rock
 lithologies at different structural levels of continental crust, arc crust, and oceanic lithosphere. Only
 a few grains yielded En values between 85 and 75. En: enstatite; Fs: ferrosilite; Wo: wollastonite.
 Colour codes similar as in Fig. 6.
- 692

693 Figure 4. Relationships among major chemical elements hosted in detrital orthopyroxenes as 694 determined by SEM-EDS. OPX from mantle harzburgites is highest in Mg, OPX from lower 695 continental and arc crust poorest in Ca. Volcanic OPX, poorer in Al, displays decreasing Mg# from 696 andesite to dacite and more felsic source rocks. Arc and rift-related volcanic OPX are not different. 697 The biplot (Gabriel, 1971) drawn using CoDaPack software by Comas-Cufí and Thió-Henestrosa, 698 2011) displays multivariate observations (points) and variables (rays). The length of each ray is 699 proportional to the variance of each element in the dataset. If the angle between two rays is close to 700 0°, 90°, and 180°, then the corresponding compositional parameters are directly correlated, 701 uncorrelated, and inversely correlated, respectively. Colour codes similar as in Fig. 6.

Figure 5. Selected Raman spectra of orthopyroxene grains from diverse source rocks in different geodynamic settings. Baseline subtraction was obtained with Labspec 5 software. Greater background noise for Cr-rich harzburgite-derived OPX is ascribed to Cr-induced fluorescence (Savel'eva et al., 2013). Peaks are stronger for more ordered OPX derived from lower-crustal granulitic metagabbro. In the low-wavelength spectral region, peaks' shape and relative intensity depends on crystal orientation.

Figure 6. Sensitivity of Raman peak positions to Mg# in detrital orthopyroxene as determined by SEM-EDS. The best correlation between peak position and Mg# is obtained for vibrational modes v3 and v4, which display excellent linear correlation with each other (middle panel to the right). Among other peaks, v_1 , v_5 , and v_6 can be used to increase the accuracy of Mg# determination, whereas v₂ is least reliable. Colour scale reflects decreasing Mg# from red (Mg# 1.0) to blue (Mg# 713 0.4).

Figure 7. Provenance determination of detrital orthopyroxene with Raman spectroscopy. The 3D plot discriminates OPX composition by using the narrow v_3 peak (correlating best with Mg#) together with v_1 (useful to assess Ca content) and the strong v_5 peak. Colour codes similar as in Fig. 6.

Table 1. Information on the 15 studied samples of orthopyroxene-rich river and beach sands
exclusively or dominantly derived from a range of mantle, deep-crustal, and volcanic rocks
generated in different geodynamic settings.

Table 2. Chemical composition of detrital othopyroxenes analyzed by SEM-EDS. Note high Si and Cr in Mg-rich OPX from mantle rocks and low Ca in OPX from lower-crustal Ivrea-Verbano metagabbros and Kohistan arc intrusives; all these OPX are Ti-poor. Fe-rich OPX from Mt. Amiata is poor in Si and Al. No distinctive features are displayed by OPX from Virunga trachytes. Mg#: Mg/(Mg+Fe) atomic ratio; En: enstatite; Fs: ferrosilite; Wo: wollastonite; b.d.l.: below detection limit.

Table 3. Mean, minimum and maximum Raman peak positions (vibrational modes v1 to v6)
distinctive of detrital othopyroxene derived from a range of mantle, deep crustal, and volcanic rocks
representing different geodynamic settings. Mg#: Mg/(Mg+Fe) atomic ratio.

Table 4. Mg# calculated from Raman peak positions. R^2 and σ Mg# represent the proportion of the variation and expected uncertainty when Mg# is derived from the value of a single Raman peak.

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733 CITED REFERENCES

734

Agostini, S., Doglioni, C., Innocenti, F., Manetti, P. and Tonarini, S. (2010) On the geodynamics of
the Aegean rift. *Tectonophysics*, 488(1-4), 7-21.

Andersen, T., Kristoffersen, M. and Elburg, M.A. (2016) How far can we trust provenance and
crustal evolution information from detrital zircons? A South African case study. *Gondwana Research*, 34,129-148.

Andò, S. (2020) Gravimetric separation of heavy minerals in sediments and rocks. *Minerals*, 10(3),
273.

Andò, S. and Garzanti, E. (2014). Raman spectroscopy in heavy-mineral studies. In *Geological Society*, London, Special Publications, **386**(1), 395-412.

- Aoki, K. I., Yoshida, T. and Jin, Y. Z. (1989) Petrology and geochemistry of Pleistocene dacitic and
 rhyolitic pyroclastic flows from southern part of northeast Honshu, Japan. *Journal of mineralogy, petrology and economic geology*, 84(1), 1-14.
- 747 Basu, A. (2017) Evolution of siliciclastic provenance inquiries: A critical appraisal. In: *Sediment*748 *Provenance, Influences on Compositional Change from Source to Sink.* 2 (eds. Mazumder, R.).
 749 Elsevier, pp. 5–23.
- Bhattacharyya, C. (1971) An evaluation of the chemical distinctions between igneous and
 metamorphic orthopyroxenes. *American Mineralogist: Journal of Earth and Planetary Materials*, 56(3-4 Part 1), 499-506.
- Bersani, D., Andò, S., Vignola, P., Moltifiori, G., Marino, I. G., Lottici, P. P. and Diella, V. (2009)
 Micro-Raman spectroscopy as a routine tool for garnet analysis. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **73**(3), 484-491.
- Bersani, D., Aliatis, I., Tribaudino, M., Mantovani, L., Benisek, A., Carpenter, M. A., Gatta, G. D.
 and Lottici, P. P. (2018) Plagioclase composition by Raman spectroscopy. *Journal of Raman Spectroscopy*, **49**(4), 684-698.
- Borromeo, L., Zimmermann, U., Andò, S., Coletti, G., Bersani, D., Basso, D., Gentile, P., Schulz,
 B. and Garzanti, E. (2017) Raman spectroscopy as a tool for magnesium estimation in Mgcalcite. *Journal of Raman Spectroscopy*, 48(7), 983-992.
- Borromeo, L., Egeland, N., Wetrhus Minde, M., Zimmermann, U., Andò, S., Madland, M. V. and
 Korsnes, R. I. (2018) Quick, easy, and economic mineralogical studies of flooded chalk for
 EOR experiments using Raman spectroscopy. *Minerals*, 8(6), 221.
- Bouysse, P., Westercamp, D. and Andreieff, P. (1990) The Lesser Antilles Island Arc. In *Proceedings of the Ocean Drilling Program, Scientific Results (eds.* Moore, J.C, Mascle, A., et
 al.) 110,4, 29-44.
- Bowen, N.L. (1935) Ferrosilite as a natural mineral. *American Journal of Science*, **5**(30), 481.
- Burns, R. G. (1966) Origin of optical pleochroism in orthopyroxenes. *Mineralogical magazine and journal of the Mineralogical Society*, **35**(273), 715-719.
- Byrne, T., Chan, Y.C., Rau, R.J., Lu, C.Y., Lee, Y.H. and Wang, Y.J. (2011) The arc–continent
 collision in Taiwan. In *Arc-continent collision*. Springer, Berlin, Heidelberg. pp. 213-245.
- Cameron, M. and Papike, J. J. (1981) Structural and chemical variations in pyroxenes. *American Mineralogist*, 66(1-2), 1-50.
- Caracciolo, L. (2020) Sediment generation and sediment routing systems from a quantitative
 provenance analysis perspective: Review, application and future development. *Earth-Science Reviews*, 209, 103226.
- Caracciolo, L., Orlando, A., Marchev, P., Critelli, S., Manetti, P., Raycheva, R. and Riley, D.
 (2016) Provenance of Tertiary volcanoclastic sediment in NW Thrace (Bulgaria): Evidence
 from detrital amphibole and pyroxene geochemistry. *Sedimentary Geology*, **336**, 120-137.
- Cawood, P.A. (1983) Modal composition and detrital clinopyroxene geochemistry of lithic
 sandstones from the New England Fold Belt (east Australia): A Paleozoic forearc terrane.

- 783 *Geological Society of America Bulletin*, **94**(10), 1199-1214.
- Colombo, A. and Tunesi, A. (1999) Alpine metamorphism of the Southern Alps west of the
 Giudicarie Line. Schweizerische Mineralogische und Petrographische Mitteilungen, 79(1),
 183-189.
- Comas-Cufí, M. and Thió-Henestrosa, F.S. (2011) CoDaPack 2.0: A Stand-Alone, Multi-Platform
 Compositional Software. In *Proceedings of the 4th International Workshop on Compositional Data Analysis*, Girona, Spain, 10–13.
- Deer, W. A., Howie, R. A., & Zussman, J. (1997) *Rock-forming minerals: single-chain silicates, Volume 2A*. Geological Society of London, London, pp.992.
- Delmonte, B., Paleari, C. I., Andò, S., Garzanti, E., Andersson, P. S., Petit, J. R., Crosta, X.,
 Narcisi, B., Baroni, C., Salvatore, M. C., Baccolo, G. and Maggi, V. (2017) Causes of dust size
 variability in central East Antarctica (Dome B): Atmospheric transport from expanded South
 American sources during Marine Isotope Stage 2. *Quaternary Science Reviews*, 168, 55-68.
- Deruelle, B. (1982) Petrology of the Plio-Quaternary volcanism of the south-central and meridional
 Andes. *Journal of Volcanology and Geothermal Research*, 14(1-2), pp.77-124.
- Dilek, Y. and Thy, P. (1998) Structure, petrology and seafloor spreading tectonics of the Kizildag
 ophiolite, Turkey. *Geological Society*, Special Publications, London, 148(1), pp.43-69.
- B00 Dilek, Y. and Newcomb, S. (2003) Ophiolite concept and its evolution. *Special Papers-Geological* B01 Society of America, 1-16.
- Bruitt, T.H., Edwards, L., Mellors, R.M., Pyle, D.M., Sparks, R.S.J., Lanphere, M., Davies, M. and
 Barreirio, B. (1999) Santorini Volcano (with a Geological map of the Santorini islands, Scale
 1/20.000). *Geological Society of London*, Memoir, **19**, 165.
- Bunkl, I., von Eynatten, H., Andò, S., Lünsdorf, K., Morton, A., Alexander, B., ... & Yoshida, K.
 (2020) Comparability of heavy mineral data–The first interlaboratory round robin test. *Earth-Science Reviews*, 211, 103210.
- B08 Dupuy, C., Dostal, J., Traineau, H. (1985) Geochemistry of volcanic rocks from Mt. Pelée,
 B09 Martinique. *Journal of volcanology and geothermal research*, 26(1-2), 147-165.
- Ebinger, C., and Furman, T. (2003) Geodynamical setting of the Virunga volcanic province, East
 Africa. *Acta Vulcanologica*, 14(1/2), 9.
- Eggler, D. H. (1986) Kimberlites: how do they form?. In *International Kimberlite Conference: Extended Abstracts*, 4, 155-159.
- Ferrari, L., Conticelli, S., Burlamacchi, L. and Manetti, P. (1996) Volcanological evolution of the
 Monte Amiata, Southern Tuscany: new geological and petrochemical data. *Acta Vulcanologica*,
 816 8, 41-56.
- Frezzotti, M. L., Tecce, F., and Casagli, A. (2012) Raman spectroscopy for fluid inclusion
 analysis. *Journal of Geochemical Exploration*, **112**, 1-20.
- Francalanci, L., Vougioukalakis, G. E., Perini, G., and Manetti, P. (2005) A West-East Traverse
 along the magmatism of the south Aegean volcanic arc in the light of volcanological, chemical
 and isotope data. In *Developments in Volcanology*, 7, Elsevier. pp. 65-111.

- Gabriel, K.R. (1971) The biplot graphic display of matrices with application to principal component
 analysis. *Biometrika*, 58, 453–467.
- Garzanti, E. (2016) From static to dynamic provenance analysis—Sedimentary petrology upgraded.
 Sedimentary Geology, **336**, 3-13.
- B26 Garzanti, E. (2019) Petrographic classification of sand and sandstone. *Earth-Science Reviews*, **192**,
 545-563.
- Garzanti, E. and Andò, S. (2007) Plate tectonics and heavy mineral suites of modern sands. In *Heavy Minerals in Use* (eds. Mange, M. and Wright, D). Elsevier, Amsterdam, Developments
 in Sedimentology, 58, 741-763.
- B31 Garzanti, E. and Andò, S. (2019) Heavy minerals for junior woodchucks. *Minerals*, **9**(3), 148.
- Garzanti, E. and Resentini, A. (2016). Provenance control on chemical indices of weathering
 (Taiwan river sands). *Sedimentary Geology*, **336**, 81-95.
- Garzanti, E., Ando, S. and Scutella, M. (2000) Actualistic ophiolite provenance: the Cyprus case.
 The Journal of Geology, **108**(2), 199-218.
- Garzanti, E., Vezzoli, G. and Ando, S. (2002a) Modern sand from obducted ophiolite belts
 (Sultanate of Oman and United Arab Emirates). *The Journal of geology*, **110**(4), 371-391.
- Garzanti, E., Canclini, S., Moretti Foggia, F. and Petrella, N. (2002b) Unraveling magmatic and
 orogenic provenance in modern sand: the back-arc side of the Apennine thrust belt,
 Italy. *Journal of Sedimentary Research*, 72(1), 2-17.
- Garzanti, E., Vezzoli, G., Andò, S., Paparella, P. and Clift, P.D. (2005) Petrology of Indus River
 sands: a key to interpret erosion history of the Western Himalayan Syntaxis. *Earth and Planetary Science Letters*, 229(3-4), 287-302.
- Garzanti, E., Ando, S. and Vezzoli, G. (2006) The continental crust as a source of sand (southern
 Alps cross section, northern Italy). *The Journal of Geology*, **114**(5), 533-554.
- Garzanti, E., Padoan, M., Andò, S., Resentini, A., Vezzoli, G. and Lustrino, M. (2013) Weathering
 and relative durability of detrital minerals in equatorial climate: sand petrology and
 geochemistry in the East African Rift. *The Journal of Geology*, **121**(6), 547-580.
- Garzanti, E., Andò, S., Limonta, M., Fielding, L., Najman, Y. (2018) Diagenetic control on
 mineralogical suites in sand, silt, and mud (Cenozoic Nile Delta): Implications for provenance
 reconstructions. *Earth-Science Reviews*, 185, 122-139.
- Garzanti, E., Capaldi, T., Vezzoli, G., Limonta, M. and Sosa, N. (2021a) Transcontinental retroarc
 sediment routing controlled by subduction geometry and climate change (Central and Southern
 Andes, Argentina). *Basin Research.* 33(6), 3406-3437.
- Garzanti, E., Limonta, M., Vezzoli, G. and Sosa, N. (2021b) From Patagonia to Río de la Plata:
 Multistep long-distance littoral transport of Andean volcaniclastic sand along the Argentine
 passive margin. *Sedimentology*, 68, 3357–3384.
- Gehrels, G. (2011) Detrital zircon U-Pb geochronology: Current methods and new opportunities. In:
 Busby, C., and Azor, A., *Tectonics of Sedimentary Basins: Recent Advances*. Blackwell,
 Oxford. pp. 47-62.

- Germa, A., Quidelleur, X., Lahitte, P., Labanieh, S. and Chauvel, C. (2011) The K–Ar Cassignol–
 Gillot technique applied to western Martinique lavas: a record of Lesser Antilles arc activity
 from 2 Ma to Mount Pelée volcanism. *Quaternary Geochronology*, 6(3-4), 341-355.
- Ghose, S., and Hafner, S. (1967) Mg2+–Fe2+ distribution in metamorphic and volcanic
 orthopyroxenes. *Zeitschrift für Kristallographie-Crystalline Materials*, **125**(1-6), 157-162.
- Greensfelder, L. (2002) Subtleties of sand reveal how mountains crumble. *Science*, 295(5553). pp. 256-258.
- Griffith, W. P. (1969) Raman studies on rock-forming minerals. Part I. Orthosilicates and
 cyclosilicates. *Journal of the Chemical Society A: Inorganic, Physical, Theoretical*, 1372-1377.
- Guo, R., Hu, X., Garzanti, E., Lai, W., Yan, B. and Mark, C. (2020) How faithfully do the
 geochronological and geochemical signatures of detrital zircon, titanite, rutile and monazite
 record magmatic and metamorphic events? A case study from the Himalaya and Tibet. *Earth- Science Reviews*, 201, 103082.
- Guo, R., Hu, X., Garzanti, E. and Lai, W. (2021) Boron isotope composition of detrital tourmaline:
 A new tool in provenance analysis. *Lithos*, 400, 106360.
- Heymann, D. (1967) On the origin of hypersthene chondrites: Ages and shock effects of black
 chondrites. *Icarus*, 6(1-3), 189-221.
- Hope, G. A., Woods, R. and Munce, C. G. (2001) Raman microprobe mineral identification. *Minerals Engineering*, 14(12), 1565-1577.
- Howie, R. A., and Smith, J. V. (1966) X-Ray-Emission Microanalysis of Rock-Forming Minerals.
 V. Orthopyroxenes. *The Journal of Geology*, 74(4), 443-462.
- Hu, X., An, W., Wang, J., Garzanti, E. and Guo, R. (2014) Himalayan detrital chromian spinels and
 timing of Indus-Yarlung ophiolite erosion. *Tectonophysics*, 621, 60-68.
- Huang, E., Chen, C. H., Huang, T., Lin, E. H. and Xu, J. A. (2000) Raman spectroscopic
 characteristics of Mg-Fe-Ca pyroxenes. *American Mineralogist*, 85(3-4), 473-479.
- Ingersoll, R.V., Bullard, T.F., Ford, R.L., Grimm, J.P., Pickle, J.D. and Sares, S.W. (1984) The
 effect of grain size on detrital modes: a test of the Gazzi-Dickinson point-counting method. *Journal of Sedimentary Petrology*, 54(1), 103-116.
- Jagoutz, O. and Schmidt, M.W. (2012) The formation and bulk composition of modern juvenile
 continental crust: The Kohistan arc. *Chemical Geology*, 298, 79-96.
- Jan, M. Q., & Howie, R. A. (1980) Ortho-and clinopyroxenes from the pyroxene granulites of Swat
 Kohistan, northern Pakistan. *Mineralogical Magazine*, 43(330), 715-726.
- Kay, S.M., Godoy, E. and Kurtz, A. (2005) Episodic arc migration, crustal thickening, subduction
 erosion, and magmatism in the south-central Andes. *Geological Society of America Bulletin*,
 117(1-2), 67-88.
- Kleiman, L.E. and Japas, M.S. (2009) The Choiyoi volcanic province at 34°S–36°S (San Rafael,
 Mendoza, Argentina): Implications for the Late Palaeozoic evolution of the southwestern
 margin of Gondwana. *Tectonophysics*, 473(3-4), 283-299.

- Kubovics, I., Ditrói Puskás, Z., and Gál-Sólymos, K. (2004). Re-evaluation of meteorites from the
 Carpathian Basin: Preliminary results from Kisvarsány, Knyahinya, Mezőmadaras, Mike, Mócs
 and Nyírábrány. *Acta Geologica Hungarica*, 47(2-3), 269-285.
- Gismelseed, A. M., Bashir, S., Worthing, M. A., Yousif, A. A., Elzain, M. E., Rawas, A. A., and
 Widatallah, H. M. (2005). Studies and characterizations of the Al Zarnkh meteorite. *Meteoritics & Planetary Science*, 40(2), 255-259.
- Kuebler, K., Wang, A., Freeman, J. J. and Jolliff, B. L. (2006). Database of Raman mineral spectra
 for planetary surface exploration. In *37th Annual Lunar and Planetary Science Conference*,
 pp.1907.
- Kuno, H. (1954). Study of orthopyroxenes from volcanic rocks. *American Mineralogist: Journal of Earth and Planetary Materials*, **39**(1-2), 30-46.
- Lai, Y.M., Song, S.R., Lo, C.H., Lin, T.H., Chu, M.F. and Chung, S.L. (2017) Age, geochemical
 and isotopic variations in volcanic rocks from the Coastal Range of Taiwan: Implications for
 magma generation in the Northern Luzon Arc. *Lithos*, 272, 92-115.
- Lebedev, V.A., Chernyshev, I.V., Chugaev, A.V., Gol'tsman, Y.V. and Bairova, E.D. (2010)
 Geochronology of eruptions and parental magma sources of Elbrus volcano, the Greater
 Caucasus: K-Ar and Sr-Nd-Pb isotope data. *Geochemistry International*, 48(1), 41-67.
- Lee, J.I., Clift, P.D., Layne, G., Blum, J. and Khan, A.A. (2003) Sediment flux in the modern Indus
 River inferred from the trace element composition of detrital amphibole grains. *Sedimentary Geology*, 160(1-3), 243-257.
- Leslie, A. G., & Nutman, A. P. (2003). Evidence for Neoproterozoic orogenesis and early high
 temperature Scandian deformation events in the southern East Greenland
 Caledonides. *Geological Magazine*, 140(3), 309-333.
- Liang, W., Garzanti, E., Andò, S., Gentile, P. and Resentini, A. (2019) Multimineral fingerprinting
 of Transhimalayan and Himalayan sources of Indus-derived Thal Desert sand (central
 Pakistan). *Minerals*, 9(8), 457.
- Limonta, M., Garzanti, E., Resentini, A., Andò, S., Boni, M. and Bechstädt, T. (2015) Multicyclic
 sediment transfer along and across convergent plate boundaries (Barbados, Lesser
 Antilles). *Basin Research*, 27(6), 696-713.
- Lindh, A. (1975) Coexisting pyroxenes—a multivariate statistical approach. *Lithos*, **8**(2), 151-161.
- 929 Lindsley, D. H. (1965) Ferrosilite. *Carnegie Institution Washington Yearbook*, **64**, 148-150.
- 930 Lippard, S.J. (1986) The ophiolite of northern Oman. *Geological Society London Memoir*, **11**,178.
- Lorenz, C. A., Ivanova, M. A., Brandstaetter, F., Kononkova, N. N., and Zinovieva, N. G. (2020).
 Aubrite Pesyanoe: Clues to composition and evolution of the enstatite achondrite parent
 body. *Meteoritics & Planetary Science*, 55(12), 2670-2702.
- Makreski, P., Jovanovski, G., Gajović, A., Biljan, T., Angelovski, D. and Jaćimović, R. (2006)
 Minerals from Macedonia. XVI. Vibrational spectra of some common appearing pyroxenes and
 pyroxenoids. *Journal of Molecular Structure*, **788**(1-3), 102-114.

- Mange, M.A. and Maurer, H.F.W. (1992) Heavy Minerals in Colour. Chapman & Hall, London,
 147.
- Mange, M.A. and Morton, A.C. (2007) Geochemistry of heavy minerals In Mange, M. & Wright,
 D. (eds.), Heavy Minerals in Use. Elsevier, Amsterdam, *Developments in Sedimentology*, 58,
 345-391.
- Marinos, V., Prountzopoulos, G., Asteriou, P., Papathanassiou, G., Kaklis, T., Pantazis, G.,
 Lambrou, E., Grendas, N., Karantanellis, E. and Pavlides, S. (2017) Beyond the boundaries of
 feasible engineering geological solutions: stability considerations of the spectacular Red Beach
 cliffs on Santorini Island, Greece. *Environmental Earth Sciences*, 76(15), 1-14.
- 946 Mason, B. (1966) The enstatite chondrites. *Geochimica et Cosmochimica Acta*, **30**(1), 23-39.
- 947 Meinhold, G. (2010) Rutile and its applications in earth sciences. *Earth-Science Reviews*, 102(1-2),
 948 1-28.
- Mernagh, T. P. and Hoatson, D. M. (1997) Raman spectroscopic study of pyroxene structures from
 the Munni Munni layered intrusion, Western Australia. *Journal of Raman Spectroscopy*, 28(9),
 647-658.
- 952 Morimoto, N. (1988) Nomenclature of pyroxenes. *Mineralogy and Petrology*, **39**(1), 55-76.
- Morse, S. A. (1975) Plagioclase lamellae in hypersthene, Tikkoatokhakh Bay, Labrador. *Earth and Planetary Science Letters*, 26(3), 331-336.
- Morton, A.C. and Hallsworth, C. (2007) Stability of detrital heavy minerals during burial
 diagenesis. In *Heavy Minerals in Use* (eds. Mange, M. and Wright, D.). Elsevier, Amsterdam, *Developments in Sedimentology*, 58. pp. 215-245.
- O'Sullivan, G., Chew, D., Kenny, G., Henrichs, I. and Mulligan, D. (2020) The trace element
 composition of apatite and its application to detrital provenance studies. *Earth-Science Reviews*, 201, 103044.
- 961 Papike, J. J., Fowler, G. W., Shearer, C. K. and Layne, G. D. (1996) Ion microprobe investigation 962 of plagioclase and orthopyroxene from lunar Mg-suite norites: implications for calculating 963 for parental melt REE concentrations and assessing postcrystallization REE 964 redistribution. Geochimica et Cosmochimica Acta, 60(20), 3967-3978.
- Pastore, G., Baird, T., Vermeesch, P., Resentini, A. and Garzanti, E. (2021) Provenance and
 recycling of Sahara Desert sand. *Earth-Science Reviews*, 103606.
- Poldervaart, A. (1947) The relationship of orthopyroxene to pigeonite. *Mineralogical Magazine and Journal of the Mineralogical Society*, 28(198), 164-172.
- Pouclet, A., Bellon, H. and Bram, K. (2016) The Cenozoic volcanism in the Kivu rift: Assessment
 of the tectonic setting, geochemistry, and geochronology of the volcanic activity in the SouthKivu and Virunga regions. *Journal of African Earth Sciences*, **121**, 219-246.
- Quick, J.E., Sinigoi, S. and Mayer, A. (1994) Emplacement dynamics of a large mafic intrusion in
 the lower crust, Ivrea-Verbano Zone, northern Italy. *Journal of Geophysical Research: Solid Earth*, 99(B11), 21559-21573.
- 875 Raman, C. V. (1928) A change of wave-length in light scattering. *Nature*, **121**(3051), 619-619.

- Ramos, V.A. and Folguera, A. (2011) Payenia volcanic province in the Southern Andes: An
 appraisal of an exceptional Quaternary tectonic setting. *Journal of Volcanology and geothermal Research*, 201(1-4), 53-64.
- Ramos, V.A. and Kay, S.M. (2006) Overview of the tectonic evolution of the southern Central
 Andes of Mendoza and Neuquén (35°–39°S latitude). In *Evolution of an Andean margin: A tectonic and magmatic view from the Andes to the Neuquén Basin (35°–39°S latitude)* (eds.
 Kay, S.M., and Ramos, V.A.). Geological Society of America Special Paper 407. pp. 1–17.
- Ramos, V.A., Cristallini, E.O. and Pérez, D.J. (2002) The Pampean flat-slab of the Central Andes. *Journal of South American Earth Sciences*, 15(1), 59-78.
- Rezvukhin, D. I., Alifirova, T. A., Korsakov, A. V. and Golovin, A. V. (2019). A new occurrence
 of yimengite-hawthorneite and crichtonite-group minerals in an orthopyroxenite from
 kimberlite: Implications for mantle metasomatism. *American Mineralogist: Journal of Earth and Planetary Materials*, **104**(5), 761-774.
- Rietmeijer, F. J. (1983) Chemical distinction between igneous and metamorphic orthopyroxenes
 especially those coexisting with Ca-rich clinopyroxenes: a re-evaluation. *Mineralogical Magazine*, 47(343), 143-151.
- Rivalenti, G., Garuti, G., Rossi, A., Siena, F. and Sinigoi, S. (1981) Existence of different peridotite
 types and of a layered igneous complex in the Ivrea Zone of the Western Alps. *Journal of Petrology*, 22(1), 127-153.
- Rogers, N.W., James, D., Kelley, S.P. and De Mulder, M. (1998) The generation of potassic lavas
 from the eastern Virunga province, Rwanda. *Journal of Petrology*, **39**(6), 1223-1247.
- Savel'eva, G. N., Batanova, V. G., Sobolev, A. V., and Kuz'min, D. V. (2013). Minerals of mantle
 peridotites: Indicators of chromium ores in ophiolites. In *Doklady Earth Sciences*, Springer
 Nature BV, 452 (1), p. 963).
- Searle, M. and Cox, J. (1999) Tectonic setting, origin, and obduction of the Oman ophiolite.
 Geological Society of America Bulletin, **111**(1), 104-122.
- Searle, M.P., Khan, M.A., Fraser, J.E., Gough, S.J. and Jan, M.Q. (1999) The tectonic evolution of
 the Kohistan-Karakoram collision belt along the Karakoram Highway transect, north Pakistan.
 Tectonics, 18(6), 929-949.
- Serri, G., Innocenti, F. and Manetti, P. (1993) Geochemical and petrological evidence of the
 subduction of delaminated Adriatic continental lithosphere in the genesis of the Neogene Quaternary magmatism of central Italy. *Tectonophysics*, 223(1-2), 117-147.
- Skridlaitė, G., Šiliauskas, L., Prušinskienė, S., & Bagiński, B. (2019). Petrography and mineral
 chemistry of the Varena Iron Ore deposit, southeastern Lithuania: implications for the
 evolution of carbonate and silicate rocks and ore mineralization. *Baltica*, 32(1), 107-126.
- Stalder, R., Kronz, A. and Schmidt, B. C. (2009) Raman spectroscopy of synthetic (Mg, Fe) SiO₃
 single crystals. An analytical tool for natural orthopyroxenes. *European Journal of Mineralogy*, 21(1), 27-32.
- 1014 Stangarone, C., Tribaudino, M., Prencipe, M. and Lottici, P. P. (2016) Raman modes in Pbca 1015 enstatite (Mg₂Si₂O₆): an assignment by quantum mechanical calculation to interpret

- 1016 experimental results. *Journal of Raman Spectroscopy*, **47**(10), 1247-1258.
- Stangarone, C., Maturilli, A., & Helbert, J. (2021, March). Calculated High Temperature Thermal IR Spectra of Orthoenstatite: Theoretical Insights on Band Shifts and Temperature. In *Lunar and Planetary Science Conference* (No. 2548, p. 2079).
- 1020 Stolper, E., and McSween Jr, H. Y. (1979) Petrology and origin of the shergottite 1021 meteorites. *Geochimica et Cosmochimica Acta*, **43**(9), 1475-1498.
- Sturm, R. (2002). PX-NOM—an interactive spreadsheet program for the computation of pyroxene
 analyses derived from the electron microprobe. *Computers & Geosciences*, 28(4), 473-483.
- Suggate, S.M. and Hall, R. (2014) Using detrital garnet compositions to determine provenance: a
 new compositional database and procedure. *Special Publications*, Geological Society, London,
 386(1), 373-393.
- Tribaudino, M., Mantovani, L., Bersani, D. and Lottici, P. P. (2011) Raman investigation on
 pigeonite in ureilite. *Spectroscopy Letters*, 44(7-8), 480-485.
- Tribaudino, M., Mantovani, L., Bersani, D. and Lottici, P. P. (2012). Raman spectroscopy of (Ca, Mg) MgSi₂O₆ clinopyroxenes. *American Mineralogist*, **97**(8-9), 1339-1347.
- Tribaudino, M., Aliatis, I., Bersani, D., Gatta, G. D., Lambruschi, E., Mantovani, L., ... and Lottici,
 P. P. (2017) High-pressure Raman spectroscopy of Ca (Mg, Co) Si₂O₆ and Ca (Mg, Co) Ge₂O₆
 clinopyroxenes. *Journal of Raman Spectroscopy*, **48**(11), 1443-1448.
- 1034Tribaudino, M., Stangarone, C., Gori, C., Mantovani, L., Bersani, D., and Lottici, P. P. (2019).1035Experimental and calculated Raman spectra in Ca–Zn pyroxenes and a comparison between1036 $(Ca_x M^{2+}_{1-x}) M^{2+}Si_2O_6$ pyroxenes $(M^{2+} = Mg, Co, Zn, Fe^{2+})$. *Physics and Chemistry of*1037*Minerals*, **46**(9), 827-837.
- 1038 Vezzoli, G., Garzanti, E., Limonta, M. and Radeff, G. (2020) Focused erosion at the core of the
 1039 Greater Caucasus: Sediment generation and dispersal from Mt. Elbrus to the Caspian
 1040 Sea. *Earth-Science Reviews*, 200, 102987.
- 1041 Viccaro, M., Giuffrida, M., Nicotra, E. and Ozerov, A.Y. (2012) Magma storage, ascent and
 1042 recharge history prior to the 1991 eruption at Avachinsky Volcano, Kamchatka, Russia:
 1043 Inferences on the plumbing system geometry. *Lithos*, 140, 11-24.
- 1044 Vincent, S.J., Somin, M.L., Carter, A., Vezzoli, G., Fox, M. and Vautravers, B. (2020) Testing
 1045 models of Cenozoic exhumation in the Western Greater Caucasus. *Tectonics*, **39**(2).
- 1046 Volynets, A. O., Churikova, T. G., Wörner, G., Gordeychik, B. N. and Layer, P. (2010) Mafic Late
 1047 Miocene–Quaternary volcanic rocks in the Kamchatka back arc region: implications for
 1048 subduction geometry and slab history at the Pacific–Aleutian junction. *Contributions to*1049 *mineralogy and petrology*, 159(5), 659-687.
- von Eynatten, H. and Dunkl, I. (2012) Assessing the sediment factory: the role of single grain
 analysis. *Earth-Science Reviews*, 115(1-2), 97-120.
- Wang, A., Jolliff, B. L., Haskin, L. A., Kuebler, K. E. and Viskupic, K. M. (2001) Characterization
 and comparison of structural and compositional features of planetary quadrilateral pyroxenes
 by Raman spectroscopy. *American Mineralogist*, **86**(7-8), 790-806.



MANTLE OPHIOLITE Kizildağ Complex	LOWER CRUST Ivrea-Verbano Zone	VOLCANIC ARC Elbrus Volcano	VOLCANIC ARC Martinique Island	VOLCANIC ARC Amiata Volcano
0		C Star		
			-	











Structural level	Geodynamic setting	Geological domain	Main lithology	Location
		Hatay-Kiziildağ Complex	Harzburgite	Hatay Peninsula (Turkey)
MANTLE		Sema'il Complex	Harzburgite	Northern Oman Mountains
	CONTINENTAL	Ivrea-Verbano Mafic Complex	Granulitic gabbro	Southern Alps (Italy)
LOWER CRUST	& ARC CRUST	Kohistan Arc	Metagabbro to granite	Northern Pakistan
		Andean Cordillera	Andesite and dacite	Río Desaguadero (Argentina)
	CONTINENTAL MAGMATIC	Andean Cordillera	Basalt to dacite	Río Grande (Argentina)
	ARC	Andean Cordillera	Basalt to dacite	Río Colorado (Argentina)
		Andean Cordillera	Dacite	Río Agrio (Argentina)
		Luzon island arc	Basalt to dacite	Taiwan Island
UPPER CRUST		Kamchatka island arc	Andesite	SE Kamchatcka (Russia)
		Lesser Antilles island arc	Andesite and dacite	Martinique Island
		South Aegean island arc	Andesite and dacite	Santorini Island (Greece)
		Mt. Amiata (Tuscan province)	Trachydacite	Orcia River (Italy)
		Elbrus Volcano	Andesite and dacite	Greater Caucasus (Russia)
	RIFT VALLEY	Virunga volcanic province	K-trachyte and latite	East African Rift (Rwanda)

setting Unit wt% wt	mol% 2.9 4.2 1.6 2.3 4.1 1.1 1.1 1.7 0.9 1.6 2.4 0.7
Near 56.6 b.d.l. 2.0 5.6 0.02 33.8 1.5 b.d.l. b.d.l. 0.8 0.92 88.9 8.3 Min 57.3 b.d.l. 2.5 5.9 0.2 34.5 2.3 b.d.l. 1.0 0.96 89.9 8.7 Min 56.0 b.d.l. 1.6 5.2 b.d.l. 33.2 0.9 b.d.l. b.d.l. 0.6 0.91 88.1 7.7 Min 56.0 b.d.l. 1.6 5.2 b.d.l. 33.2 0.9 b.d.l. b.d.l. 0.6 0.91 88.1 7.7 Max 56.6 0.4 3.3 8.8 0.4 33.3 2.1 0.3 0.4 1.4 0.94 88.4 13.9 Min 54.3 0.2 0.8 5.8 0.2 31.6 0.6 b.d.l. 0.08 0.7 0.87 84.9 9.3	2.9 4.2 1.6 2.3 4.1 1.1 1.7 0.9 1.6 2.4 0.7
Nin 56.0 b.d.l. 2.5 5.9 0.2 34.5 2.3 b.d.l. 1.0 0.96 89.9 8.7 Min 56.0 b.d.l. 1.6 5.2 b.d.l. 33.2 0.9 b.d.l. b.d.l. 0.6 0.91 88.1 7.7 Mean 55.4 0.3 2.2 6.8 0.3 32.2 1.2 0.1 0.3 1.1 0.91 88.1 7.7 Max 56.6 0.4 3.3 8.8 0.4 33.3 2.1 0.3 0.4 1.4 0.94 88.4 13.9 Min 54.3 0.2 0.8 5.8 0.2 31.6 0.6 b.d.l. 0.08 0.7 0.87 84.9 9.3	4.2 1.6 2.3 4.1 1.1 1.7 0.9 1.6 2.4 0.7
Min 56.0 b.d.l. 1.6 5.2 b.d.l. 33.2 0.9 b.d.l. b.d.l. 0.6 0.91 88.1 7.7 Hean 55.4 0.3 2.2 6.8 0.3 32.2 1.2 0.1 0.3 1.1 0.91 88.1 10.7 Max 56.6 0.4 3.3 8.8 0.4 33.3 2.1 0.3 0.4 1.4 0.94 88.4 13.9 Min 54.3 0.2 0.8 5.8 0.2 31.6 0.6 b.d.l. 0.08 0.7 0.87 84.9 9.3	1.6 2.3 4.1 1.1 1.7 0.9 1.6 2.4 0.7
Mean 55.4 0.3 2.2 6.8 0.3 32.2 1.2 0.1 0.3 1.1 0.91 87.0 10.7 Sema'il Max 56.6 0.4 3.3 8.8 0.4 33.3 2.1 0.3 0.4 1.4 0.94 88.4 13.9 Min 54.3 0.2 0.8 5.8 0.2 31.6 0.6 b.d.l. 0.08 0.7 0.87 84.9 9.3	2.3 4.1 1.1 1.7 0.9 1.6 2.4 0.7
B Sema'il Max 56.6 0.4 3.3 8.8 0.4 33.3 2.1 0.3 0.4 1.4 0.94 88.4 13.9 Min 54.3 0.2 0.8 5.8 0.2 31.6 0.6 b.d.l. 0.08 0.7 0.87 84.9 9.3	4.1 1.1 1.7 0.9 1.6 2.4 0.7
Min 54.3 0.2 0.8 5.8 0.2 31.6 0.6 b.d.l. 0.08 0.7 0.87 84.9 9.3	1.1 1.7 0.9 1.6 2.4 0.7
	1.1 1.7 0.9 1.6 2.4 0.7
⊣⊢ Mean 52.6 0.02 2.4 21.4 0.6 22.2 0.5 b.d.l. 0.02 b.d.l. 0.65 63.4 35.5	1.7 0.9 1.6 2.4 0.7
إلى الاتفاد الاتفاد الاتفاد العام المعام ا	0.9 1.6 2.4 0.7
шё Мin 51.3 b.d.l. 1.6 16.3 0.4 17.6 0.4 b.d.l. b.d.l. b.d.l. 0.53 51.9 26.1	1.6 2.4 0.7
Mean 51.5 b.d.l. 1.7 24.3 0.5 20.4 0.8 b.d.l. b.d.l. b.d.l. 0.61 58.5 40.0	2.4 0.7
$\overline{O} \overset{\triangleleft}{\triangleleft}$ Kohistan Max 52.7 b.d.l. 2.2 25.9 0.8 21.4 1.1 b.d.l. b.d.l. b.d.l. 0.63 60.7 43.3	0.7
Min 50.9 b.d.l. 1.0 23.1 0.3 18.7 0.4 b.d.l. b.d.l. b.d.l. 0.57 54.3 37.6	
Río Mean 53.9 0.6 1.2 18.0 0.3 24.5 1.6 0.2 0.3 0.02 0.73 68.3 28.5	3.2
Desaguadero Max 56.2 0.8 2.7 21.1 0.5 30.8 2.0 0.4 0.5 0.5 0.88 82.9 33.7	4.2
	2.0
E Río Grande Mean 54.7 0.5 0.9 17.1 0.4 23.2 1.5 0.2 0.4 b.d.l. 0.69 66.7 30.2	3.1
$\Delta = \begin{bmatrix} A \ B \ C \ C \ C \ C \ C \ C \ C \ C \ C$	3.9
Min 53.5 0.3 0.2 15.7 0.2 21.1 1.0 0.1 0.2 b.d.l. 0.64 61.3 25.2	2.2
Río Colorado Mean 53.9 0.2 0.7 18.6 0.9 24.1 1.6 b.d.l. 0.3 0.02 0.71 66.7 30.3	3.1
Max 55.1 0.4 1.3 22.0 1.7 26.3 2.4 b.d.l. 0.6 0.3 0.80 71.3 35.6	4.8
Min 53.1 0.1 0.5 15.4 0.5 21.5 1.1 b.d.l. 0.2 b.d.l. 0.65 61.4 24.3	2.2
Z Mean 53.0 0.4 0.7 24.8 0.6 18.8 1.5 b.d.l. 0.3 b.d.l. 0.58 55.1 41.7	3.2
O (Argentina) Max 54.9 0.7 2.4 27.0 1.1 24.8 2.0 b.d.l. 0.8 b.d.l. 0.74 71.2 44.2	4.2
Min 50.7 0.2 0.3 15.3 0.3 17.5 1.3 b.d.l. 0.05 b.d.l. 0.55 52.9 25.1	2.5
Mean 53.2 0.4 1.2 18.2 0.5 24.8 1.5 0.1 0.2 0.3 0.73 68.2 28.9	2.9
Taiwan Max 54.2 0.5 1.7 20.1 0.7 27.5 2.0 0.2 0.4 0.5 0.83 74.9 31.7	3.8
Min 52.0 0.2 0.7 13.4 b.d.l. 23.6 0.8 b.d.l. 0.09 b.d.l. 0.70 65.4 21.2	1.6
Mean 52.5 0.4 1.4 17.9 0.4 25.0 1.6 0.2 0.2 0.09 0.75 68.7 28.2	3.1
Kamchatka Max 53.5 0.6 2.4 21.1 0.7 26.3 2.0 0.3 0.4 0.2 0.80 71.7 34.2	4.0
Min 51.5 0.3 0.6 15.9 0.2 22.7 1.0 0.04 0.1 b.d.l. 0.68 63.5 24.6	2.1
Mean 50.5 0.4 0.9 26.1 1.2 19.4 1.4 b.d.l. 0.2 0.3 0.61 54.2 43.0	2.8
꽃 Martinique _{Max} 53.4 0.7 1.8 29.4 1.5 21.9 1.6 b.d.l. 0.4 0.5 0.69 59.3 48.1	3.2
Min 48.4 0.2 0.3 23.5 0.8 17.3 0.9 b.d.l. b.d.l. 0.1 0.53 49.2 37.7	1.7
Mean 51.0 0.4 0.8 22.7 0.9 22.4 1.6 0.1 0.2 0.01 0.66 59.9 36.9	3.2
Santorini Max 53.6 0.6 1.3 26.7 1.4 43.5 2.2 0.2 0.3 0.07 0.72 66.4 44.9	4.4
> Min 50.7 0.3 b.d.l. 16.1 0.3 18.2 0.4 0.05 b.d.l. b.d.l. 0.58 52.1 19.2	0.5
Mean 49.8 0.4 0.6 32.0 0.4 14.7 1.5 0.2 0.1 b.d.l. 0.47 43.3 53.6	3.1
Amiata Max 51.5 0.7 1.4 35.0 0.7 17.0 1.8 0.4 0.4 b.d.l. 0.54 49.3 57.9	3.7
Min 48.5 b.d.l. b.d.l. 28.6 0.2 13.2 1.1 b.d.l. b.d.l. 0.41 38.9 47.3	2.4
Mean 54.2 0.4 1.3 17.2 0.5 25.7 1.3 b.d.l. b.d.l. 0.2 0.73 70.2 27.3	2.5
Elbrus Max 55.1 0.4 2.6 21.7 0.8 29.0 1.6 bdl bdl 0.5 0.81 77.7 34.9	31
Min 52.8 0.2 0.5 12.5 0.3 22.9 10 bdl bdl bdl 0.65 63.3 192	1.9
Main 62.0 0.2 0.0 22.0 1.0 50.01 50.01 60.0 60.0 70.2	3.4
$\Box = \Box$ Virunga Max 52.9 0.5 1.1 25.6 0.3 22.8 1.8 b.d.l. 0.3 0.3 0.69 64.8 42.1	3.6
Min 51.4 0.4 0.5 19.7 0.2 18.7 1.5 b.d.l. 0.2 b.d.l. 0.57 54.6 31.8	3.2

Geodynamic	Unit	Ma#		v ₁	v ₂	V ₃	V ₄	v ₅	V ₆
setting		0		cm ⁻¹	cm⁻¹	cm⁻¹	cm ⁻¹	cm⁻¹	cm⁻¹
		0.92	Mean	343.4	400.8	662.1	683.8	1011.5	1030.
Сш	Kiziildağ	0.96	Max	344.3	402.3	662.7	684.6	1012.9	1031.
걸린		0.91	Min	342.1	398.5	661.4	683	1010.1	1028.
AN HIG		0.91	Mean	343.5	400.5	661.9	683.9	1010.3	1030.
	Sema'il	0.94	Max	345.0	403.8	662.8	684.9	1012.6	1033.
		0.87	Min	341.2	397.8	661.2	683.3	1009.7	1027.
- <u> </u> -		0.65	Mean	335.9	393.6	654.8	675.6	1000.1	1014.
US	Ivrea-Verbano	0.75	Max	340.8	402.1	658.0	679.4	1004.2	1022.
CRI		0.53	Min	332.5	384.2	652.4	672.1	996.7	1007.
ULL O		0.61	Mean	334.7	389.8	654.6	674.3	999.3	1013.
AR	Kohistan	0.63	Max	336.7	399.2	656.2	676.0	1001.0	1021.
Ŭ ∞		0.57	Min	332.2	382.0	652.7	672.5	997.6	1009.4
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~		0.73	Mean	333.7	394.4	656.1	675.8	1003.8	1021.
RO	Río Desaguadero	0.88	Max	340.9	401.1	660.0	681.6	1007.8	1030.
<ul><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li><li></li></ul>	(Argentina)	0.66	Min	331.0	387.3	654.1	673.5	1001.5	1016.
TT/		0.69	Mean	331.8	393.0	655.3	674.6	1002.9	1019.
W.	Río Grande	0.74	Max	335.7	397.4	657.4	676.6	1005.2	1024.4
IAG	(Argentina)	0.64	Min	326.6	387.9	652.8	672.0	1000.3	1016
≥ ⊣		0.71	Mean	332.9	394.5	655.9	675.3	1003.1	1018.
TA	Río Colorado	0.80	Max	335.1	403.4	657.7	677.2	1005.0	1022
Z U	(Argentina)	0.65	Min	330.5	390.0	654.3	673.3	1001.2	1012
NIL N		0.58	Mean	329.6	390.2	653.3	672.5	1000.9	1015
NC	Río Agrio	0.74	Max	336.4	397.6	656.8	677.5	1005.2	1023
ŏ	(Argentina)	0.55	Min	328 1	386.8	652.6	671.6	000.2	1020.
		0.00	Mean	333.8	395.0	656.4	676.2	1003.6	1010.
	Taiwan	0.83	Max	336.2	300.5	658.2	678.1	1005.0	1024
	raiwan	0.00	Min	326.4	302 1	655.5	675.1	1000.0	1024.
		0.70	Moon	222.5	302.4	656.0	675.7	1002.5	1071.
	Kamchatka	0.75	Max	336.3	393.0 308.0	657 A	677 /	1005.0	1021.
	Ramonatka	0.00	Min	220.0	280.2	652.0	672.2	1005.5	1020.
		0.00	Moon	329.0	200.5	653.0	672.2	1001.4	1010.
RC	Martiniqua	0.01	Mox	323.3 222.0	390.3	655.0 655.1	674.0	1000.0	1014.
A O	Martinique	0.09	Min	22.0	205 7	652.0	670.0	009.2	1019.0
NN/		0.53	IVIII I Maan	320.0	300.7	654.0	672.4	990.3	1011.0
^C	Santarini	0.00	wean	330.0	392.1	<b>634.2</b>	073.4	1001.8	1010.4
0I	Santonni	1.00	IVIAX	334.2	402.4	660.8	070.0	1006.7	1022.0
		0.58	IVIIN	327.9	386.9	651.4	070.8	999.7	1013.0
	Aminto	0.47	wean	324.9	384.8	650.0	668.7	996.6	1010.4
	Amiata	0.54	Max	328.3	395.3	651.7	670.2	997.5	1016.9
		0.41	Min	322.1	377.1	648.9	667.5	995.8	1001.4
	<b>_</b> "	0.73	Mean	333.5	395.7	655.9	675.8	1002.6	1019.
	Elbrus	0.81	Max	339.1	400.9	659.3	680.0	1006.5	1024.
		0.65	Min	326.7	387.7	652.6	671.9	999.7	1008.
ĿЩ		0.63	Mean	331.1	390.8	654.1	673.1	1000.9	1016.
ALL ALL	Virunga	0.69	Max	332.5	395.7	655.6	674.6	1004.5	1021.0
- >		0.57	Min	328.9	386.8	652.5	671.7	999.2	1012.0

Vibrational modes	Equations (cm ⁻¹ )	R ²	σMg#
v ₁ (~ 330 cm ⁻¹ )	Mg# = (v ₁ – 309.0) / 34.9	0.8	0.19
v ₂ (~ 395 cm ⁻¹ )	Mg# = (v ₂ - 372.0) / 31.3	0.52	0.31
v ₃ (~ 655 cm⁻¹)	Mg# = (v ₃ – 639.5) / 23.2	0.88	0.15
v₄ (~ 675 cm⁻¹)	Mg# = (v ₄ – 655.1) / 29.2	0.88	0.13
v ₅ (~ 1002 cm ⁻¹ )	Mg# = (v ₅ – 984.5) / 26.5	0.85	0.16
v ₆ (~ 1020 cm ⁻¹ )	$Mg# = (v_6 - 989.9) / 42.4$	0.72	0.21