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Lead isotope systematics in ophiolite-associated sulphide deposits from the Western Alps and Northern Apennine (Italy)

Running title: Lead isotopes in ophiolite-associated sulphide deposits

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Lead isotope systematics in ophiolite-associated sulphide deposits from the Western Alps and Northern Apennine (Italy)

Abstract: We report Multi-Collector-ICP-MS analyses of Pb isotopes for hydrothermal deposits in ophiolitic units of the Western Alps (hereafter, WA) and Northern Apennine (hereafter, NA). The deposits include (i) volcanogenic massive sulphides formed on the seafloor of the Mesozoic Piemonte–Liguria ocean, which were subjected to subduction- (blueschist to eclogite facies) and collision-related (greenschist facies) metamorphism during the Alpine orogenesis (WA) or escaped Alpine metamorphism (NA), and (ii) post-collision veins cutting the metamorphic oceanic units. The unmetamorphosed sulphides have a MORB-like Pb isotope signature. Sulphides that re-crystallised under eclogitic conditions incorporated an old continental Pb component, which was released from gangue minerals or neighbouring sediments by dehydration reactions at the blueschist–eclogite transition. Our data suggest a limited mobility of sulphide-hosted metals in the subducted oceanic crust up to eclogite-facies conditions. Sulphides in the blueschist-facies and, possibly, eclogite-facies units incorporated further continental Pb derived from oceanic metasedimentary host-rocks containing a continent-sourced terrigenous component during subsequent greenschist-facies metamorphism. Some of the post-collision veins show isotopic similarity with the massive sulphides contained in the same ophiolitic units, suggesting derivation of metals from similar sources (*i.e.*, ophiolites and/or associated metasediments). In the Saint-Véran syn-metamorphic vein deposit, a complex Pb isotope pattern suggests mixing of fluids derived from local retrogressed blueschist-facies rocks with farther-travelled fluids discharged by or reacted with deeper, eclogitic units.

Keywords: Western Alps; Northern Apennine; Piemonte Zone; lead isotopes; metamorphism; subduction; massive sulphides; metallogeny

1. Introduction

Subduction processes that take place at convergent margins are among the most important mechanisms for the cycling of metals in the Earth (*e.g.*, Tatsumi & Kogiso, 2003). In particular, the relatively small-volume massive sulphide deposits that are typically formed by hydrothermal processes on the ocean seafloor (*e.g.*, Rona & Scott, 1993) have been inferred to contribute significantly to the total mass of sulphide-associated elements (*e.g.*, Cu, Zn, Pb and Au) that can be transferred to the continental crust via subduction and arc volcanism (Peuker-Ehrenbrink *et al.,* 1994). Many of these sulphide deposits are now found in ophiolitic units that mark the suture zones of collisional belts (*e.g.*, Galley & Koski, 1999; Franklin *et al.,* 2005; Herrington *et al.,* 2005). In some cases, their host-rocks recorded a metamorphic history of subduction to high-pressure conditions and subsequent exhumation (*e.g.*, Dal Piaz & Omenetto, 1978; Russell *et al.,* 2000; Martin *et al.,* 2008; Rebay & Powell, 2012; Giacometti & Rebay, 2013). The study of these ophiolite-hosted sulphide deposits can thus provide useful constraints for understanding metal and fluid mobility in subduction zones and collisional orogens.

Analysis of Pb isotopes is one of the most widely used methods for discrimination of the geological sources of Pb, and by inference of other metals, and of the fluid pathways in mineral deposits (*e.g.*, Tosdal *et al.,* 1999). Application of this method in metamorphic terrains is not always straightforward, because detailed plumbotectonic models may not be available for the specific geological province and regional-scale overprinting by syn- or post-metamorphic magmatic or hydrothermal events can induce isotopic changes or even homogenisation within deposits of different age or type (*e.g.*, Marshall & Spry, 2000). Nonetheless, in several instances Pb isotope data have provided useful indications on the role of metamorphic processes in the formation, evolution and upgrade of ore deposits (*e.g.*, Carr *et al.,* 1995; Pettke & Frei 1996; Marshall & Spry, 2000; Heinrich *et al.,* 2000).

In the present contribution, we investigate Pb isotope compositional variations in Cu (± Zn, Ni, Co, Au)-bearing sulphide deposits from ophiolitic units of the Western Alps (hereafter, WA) and Northern Apennine (hereafter, NA). These deposits have recorded processes of metal concentration and redistribution during the opening of the Piemonte–Liguria segment of the Mesozoic Tethyan ocean and the subsequent Late Cretaceous–Cenozoic Alpine orogenic cycle. Our previous isotopic data for these deposits (Artioli *et al.,* 2009) will be refined, integrated with new data and compared with existing Pb isotope data for rocks from WA oceanic and continental units. The results will be used (i) to identify the possible geological sources of Pb, and (ii) to assess the role of specific metallogenic processes and Alpine metamorphism in the development and modification of the isotopic signatures of the deposits.

2. Geological outline

The Alps are a double-vergent collisional belt that was developed by subduction of a Tethys-related Mesozoic ocean (Piemonte–Liguria ocean) and subsequent collision between the Adria and Europe continental plates (*e.g.*, Dal Piaz *et al.,* 2003, and references therein). The core of the Europe-vergent belt consists of the metamorphic Austroalpine–Penninic wedge, a subduction-collisional complex of Late Cretaceous–Early Oligocene age containing remnants of the Piemonte–Liguria oceanic lithosphere (Piemonte Zone, hereafter PZ) and of its passive continental margins (*e.g.*, Dewey *et al.,* 1973; Dal Piaz, 1974a,b, 1999; Lemoine *et al.,* 1987; Stampfli *et al.,* 1998; Beltrando *et al.,* 2010, 2014). The Adria-vergent belt (Southern Alps) is a non-metamorphic thrust-and-fold retro-belt, which developed probably since the Late Cretaceous within the Adria upper plate (Schumacher *et al.,* 1997) (Fig. 1).

In the WA, the ophiolite-bearing PZ tectonically overrides continental units, which were derived from different portions of the European margin, *i.e.*, the middle-Penninic Briançonnais composite nappe system to the west (*e.g.*, Escher *et al.,* 1997; Malusà *et al.,* 2005), and the inner-Penninic Dora–Maira, Gran Paradiso and Monte Rosa continental basement nappe systems (*i.e.*, the Internal Crystalline Massifs) to the east (*e.g.*, Elter, 1972; Dal Piaz, 1974a,b, 2001) (Fig. 1). The PZ is then overlain by and partly tectonically interleaved with portions of the original distal Adria margin, represented by the Austroalpine Sesia inlier and Dent Blanche nappe and by other minor continental allochthons (Dal Piaz *et al.*, 2003) (Fig. 1).

Further remnants of the Piemonte–Liguria ocean are found in the more southerly Apennines, a single-vergent orogen which was formed by the late Eocene–Oligocene subduction of the Adria plate along the south-western prolongation of the Alpine retro-belt (Carminati & Doglioni, 2012). During this tectonic phase, in the NA, the previously formed, ophiolite-bearing, oceanic accretionary prism (Ligurides) and its sedimentary cover progressively overrode the Adriatic units and escaped Alpine metamorphism (Treves, 1984; Principi & Treves, 1984; Marroni *et al.,* 2010; and references therein) (Fig. 1).

2.1 The PZ and NA ophiolites

In the PZ, two main groups of ophiolitic units can be recognised, which are characterised by different lithostratigraphic setting and high-pressure metamorphic histories (Fig. 1): i) the *blueschist-facies units* are carbonatic to terrigenous flysch-type metasediments (calcschists s.l.), which are often interleaved with metabasalts and contain olistoliths and tectonic slices of metabasalts, metagabbros and ultramafic rocks (Lombardo & Pognante, 1982; Lemoine *et al.,* 1987); ii) the *eclogitic units* are antigorite serpentinites intruded by discontinuous metagabbro bodies, and overlain by metabasalts, manganiferous metacherts, impure marbles, syn-orogenic deposits, and subduction mélanges (*e.g.*, Dal Piaz & Ernst, 1978). The main blueschist units include, from north to south, the Combin Zone and the Queyras Schistes Lustrés; the main eclogitic units include the tectono-stratigraphically lower Zermatt–Saas Zone and its south extension to the Monviso and Voltri massifs (Fig. 1).

Modern reported ages for the eclogitic peak (^{39}Ar/^{40}Ar on white mica, U–Pb on zircon and Lu–Hf on garnets) are mostly clustered at 46±3 Ma (*cf*. review in Beltrando et al., 2010, and additional data in Villa *et al.,* 2014). Geochronological data for the blueschist-facies peak overlap with those for the eclogite peak, but are more scattered (62–40 Ma, ^{39}Ar/^{40}Ar; Takeshita *et al.,* 1994; Agard *et al.,* 2002). Radiometric and biostratigraphic formation ages for the magmatic and sedimentary oceanic units range from ca. 170 to ca. 150 Ma (see review in Lombardo *et al.,* 2002, and additional data in Rubatto & Hermann, 2003).

Estimated conditions for the peak of metamorphism in different blueschist-facies units are in the range 300–500 °C and 1.0–2.0 GPa (Agard *et al.,* 2000, 2001; Cartwright & Barnicoat, 2002; Bousquet *et al.,* 2008; Giacometti & Rebay, 2013). Those for the eclogitic Zermatt–Saas Zone are of ca. 530 to 630 °C and ca. 2.1 to >3.2 GPa (Bucher *et al.,* 2005; Martin *et al.,* 2008; Li *et al.,* 2008; Angiboust *et al.,* 2009; Groppo *et al.,* 2009; Rebay & Powell, 2012; Rebay *et al.,* 2012). Both the blueschist and the eclogitic units were variably overprinted by a common, collision-related, greenschist-facies metamorphism (Ballèvre & Merle, 1993; Dal Piaz, 1999) of Late Eocene–mid Oligocene age (Hunziker *et al.,* 1992).

In addition, before the Alpine orogeny, the ophiolitic bodies underwent different degrees of oceanic hydrothermal alteration (Bonatti *et al.,* 1976), which is presently documented by hydrated lithologies containing chlorite, glaucophane, lawsonite pseudomorphs and lizardite-antigorite, and by albite-rich metabasalts and metasediments. A U-Th-Pb age of ca. 150 Ma was determined on uraninite for a serpentinite-hosted magnetite deposit interpreted as the deep segment of an oceanic hydrothermal system, possibly connected with seafloor massive sulphide deposits (Toffolo *et al.,* 2017).

The distinctive tectono-stratigraphic associations represented by the eclogite-facies and blueschist-facies PZ units are broadly reproduced in the non-metamorphic NA, where two main oceanic domains are distinguished (External and Internal Ligurides, respectively; Abbate *et al.,* 1994, and references therein) (Fig. 1): the sediment-rich, ophiolite-bearing External Ligurides resemble the calcschist-dominated association of the blueschist-facies PZ, whereas the ophiolite-rich Internal Ligurides may be correlated with the ophiolite-rich eclogitic association of the PZ (Dal Piaz *et al.,* 2003). In both domains, an oceanic hydrothermal alteration is documented by the presence of variable amounts of serpentine, chlorite, albite, clays and epidote (Cortesogno *et al.,* 1975; Zaccarini & Garuti, 2008).

3. Studied deposits and sample materials

The deposits studied here are (i) Cu (± Zn)-bearing volcanogenic massive sulphide (hereafter VMS) deposits, which were formed on the seafloor of the Jurassic Piemonte–Liguria ocean and were (PZ) or were not (NA) subjected to Alpine metamorphism, and (ii) syn- to post-metamorphic, post-collision, Cu (± Zn, Co, Ni)-bearing hydrothermal veins cutting the same oceanic units that are host to the PZ VMS deposits. A list of the deposits and of their main features is provided in Table 1 and their location is shown in Fig. 1. More detailed geological outlines and mineralogical descriptions are given in the Supplementary Appendix. Some of the samples considered for this research had previously been investigated for Pb isotopes during the archaeological work of Artioli *et al.* (2009), in which simplified descriptions of the minerals analysed were provided. Many of the samples studied by Artioli *et al.* (2009) have been re-examined in detail and more thorough mineralogical descriptions are given in the Supplementary Appendix and summarised in Tables 1 and S1. Some samples of secondary Cu minerals, which were studied by Artioli *et al.* (2009) and were formed during recent supergene processes, were strongly enriched in radiogenic Pb (*e.g.*, ^{206}Pb/^{204}Pb up to 24.53, ^{207}Pb/^{204}Pb up to 15.89) relative to the primary minerals from the same deposit. These samples probably contain radiogenic Pb derived from recent weathering of surrounding U-bearing rocks and have not been considered for the present work. The absence of weathering products associated with aberrant isotopic compositions in the selected samples ensures that their primary isotopic signature was not modified by supergene processes. The selected samples were analysed for lead isotope (Multi-Collector-ICP-MS) and trace elements (ICP-MS). Details on sample preparation and analysis are given in the Supplementary Appendix.

4. Results

4.1 Trace elements

The ore samples from the NA and PZ VMS deposits show geochemical features typical of VMS deposits from (ultra)mafic settings (*cf.* Fouquet *et al.,* 2010; Melekestseva *et al.,* 2013, 2017), such as relatively high Zn (median = 505 ppm) and Se (119 ppm), moderately high Co (50 ppm), Ni (77 ppm), Ag (46 ppm) and As (21 ppm), comparatively low Pb (54 ppm) and locally significant concentrations of Au (1 ppm, up to 18 ppm) (Table S2). The variable concentrations of many of these elements in the studied samples (Table S2) mostly reflect the variable proportions of the different minerals in the sulphide separates rather than a significant within-deposit or inter-deposit variability. The Ni/Co ratios for the most pyrite-rich samples are lower than unity, consistent with their 'mafic' seafloor signature (*cf.* Zaccarini & Garuti, 2008; Melekestseva *et al.,* 2013, 2017). The higher Ni/Co ratios shown by the samples from the eclogite-facies and a few other VMS deposits may reflect the higher proportion of chalcopyrite in the separates (*cf.* Table S1 and S2). This is consistent with the strong partitioning of Co in pyrite relative to chalcopyrite in the ores, whereas Ni concentrations are similar in these two minerals (Fantone *et al.,* 2014).

The ore samples from the post-collision veins show much larger compositional variations (Table S2), which in part reflect their very different mineralogy. The bornite- or chalcopyrite-rich Saint-Véran samples still show broad similarities with the VMS deposits, but are characterised by relatively low Co (median = 27 ppm), relatively high Ni (136 ppm), steady concentrations of Te (19 ppm) and locally high concentrations of Pb (up to 2400 ppm). The Cruvino and Usseglio vein samples have the highest As (0.4 and 16 wt%, respectively) and Sb contents (0.2 and 4.2 wt%), which reflect the presence of abundant tetrahedrite–tennantite ± arsenopyrite and Ni-arsenides. Ore samples from both veins also exhibit relatively high Bi (386 and 162 ppm, respectively) and significant Au concentrations (28 and 3 ppm, respectively). The high Ba content in the Usseglio sample reflects the presence of barite in the analysed separate.

The Th and U contents mostly vary between a few ppm to below the detection limits in all types of deposits. Exceptions are samples M/U 9748 (Cruvino) and BOM1 (Boccassuolo), with over 10 ppm of U and, respectively, Th.

4.2 Lead isotopes

4.2.1 Effect of age-correction

The Pb isotope ratios were corrected for time-integrated decay of ^{235,238}U and ^{232}Th (closed system), using U, Th and Pb concentrations obtained by ICP-MS analysis (Table S1). Corrections were calculated at times that may correspond to or provide upper limits for isotopic closure, *i.e.*, the maximum reported age of the oceanic stage (170 Ma) for the VMS deposits, the maximum age of high-pressure metamorphism (62 Ma) for the Saint-Véran syn-metamorphic vein, and the maximum age of the greenschist-facies overprint (36 Ma) for the post-metamorphic veins (*e.g.*, Lombardo *et al.,* 2002; Beltrando *et al.,* 2010; and references therein). The effect of corrections is generally minimal, despite the fact that ages used for calculations were often maximum ages and may thus have caused overcorrections (Table S1; Figs. 2–4). This may be particularly relevant for the metamorphosed VMS deposits, in which isotopic resetting may have occurred during the Paleocene(?)-Eocene high-pressure metamorphism or during the subsequent Eocene–Oligocene greenschist facies overprint. Only for two NA samples (BOM1 and LOR_Bp1) the correction effects were major, but for at least one of them the resulting ^{206}Pb/^{204}Pb ratio was unreasonably low (Fig. 2), suggesting overcorrection due to recent U addition (see below). This hypothesis is supported by the fact that the uncorrected data for these two samples appear to be much more similar to corrected or uncorrected data for other samples from the same group of deposits (Fig. 2).

Age-correction could not be calculated for a few samples that were not analysed for trace elements. Nonetheless, their uncorrected Pb isotope ratios appear to be similar to, or to fall on similar trends as, age-corrected data for the same deposits or from the same group of deposits (Table S1; Figs. 2–4). This suggests that the uncorrected data may safely be used for comparative purposes. When considering these data, however, the possible effect of closed-system radioactive decay of ^{235,238}U and ^{232}Th on Pb isotope ratios will be discussed.

4.2.2 The isotopic groups

The ophiolite-associated VMS deposits of the PZ and NA show large Pb isotope variations (Table S1 and Fig. 2 and 3). These variations are best described if deposits characterised by different Alpine metamorphic overprint are distinguished.

The clean sulphide separates from the *unmetamorphosed* VMS deposits associated with the NA ophiolites show relatively non-radiogenic Pb isotope ratios (Fig. 2). The effect of age-correction at up to 170 Ma, *i.e.*, the maximum estimated age of the protoliths of the host ophiolitic complexes and of related seafloor hydrothermal systems, is generally minimal. One major exception is a very Pb-poor sample from M. Loreto (sample LOR_M2prph; Table S1), which suggests recent addition of external U after sulphide deposition, possibly by remobilisation of primary uraninite (*cf.* Garuti & Zaccarini, 2005). The unrefined, gangue-bearing samples show a distinct trend towards higher ^{207}Pb/^{204}Pb ratios relative to the isotopically more uniform, clean sulphide separates from the same deposits (Fig. 3). The shift of these gangue-bearing samples is particularly evident if their isotopic composition is compared with that of clean sulphide separates from the same samples.

The *blueschist-facies* VMS deposits of the PZ partly overlap with the unmetamorphosed NA deposits, but they define a trend of progressively more radiogenic compositions characterised by increasing ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios (Fig. 2). Analyses of multiple samples from individual deposits indicate significant within-deposit variations along the same isotopic trend (Fig. 2). In particular, the two samples of remobilised chalcopyrite from the Alagna deposit are significantly more radiogenic (*e.g.*, ^{206}Pb/^{204}Pb = 18.241–18.522) than the pyrite sample from the same deposit (^{206}Pb/^{204}Pb = 17.863). Nonetheless, if one considers the blueschist-facies VMS group as a whole, no systematic variation is observed between pyrite-rich samples (^{206}Pb/^{204}Pb = 17.863–18.838) and chalcopyrite-rich samples (^{206}Pb/^{204}Pb = 18.177–18.753; Table S1).

The *eclogite-facies* VMS deposits of the PZ show a distinct isotopic pattern characterised by more uniform ^{207}Pb/^{204}Pb and slightly variable ^{206}Pb/^{204}Pb ratios, lying above the 'young upper crust' growth curve of Kramers & Toltsikhin (1997) (Fig. 2). Post-metamorphic hydrothermal veins in the eclogitic PZ (Cruvino, Usseglio, La Reale) have similar ^{207}Pb/^{204}Pb ratios, but are, on average, more radiogenic (Fig. 4). Only part of the isotopic variability within this 'eclogitic' group can be ascribed to post-deposition closed-system decay of ^{235,238}U and ^{232}Th, as in several cases the effect of age-correction is negligible (Table S1; Fig. 2 and 4). No systematic isotope variation is observed between pyrite-rich and chalcopyrite-rich samples (Table S1).

The Saint-Véran vein deposit from the Queyras blueschist PZ shows very large isotopic variability (Fig. 4). The four bornite ± sphalerite samples have relatively low ^{206}Pb/^{204}Pb ratios, broadly comparable to those of the unmetamorphosed VMS deposits associated with the NA ophiolites. However, their ^{207}Pb/^{204}Pb ratios are highly variable, reaching the values of the eclogite-facies deposits. The two chalcopyrite samples have higher ^{206}Pb/^{204}Pb ratios and fall close to the blueschist-facies VMS trend. The two malachite samples have compositions similar to those of average bornite and chalcopyrite, respectively.

5. Discussion

5.1 The seafloor isotopic heritage

The Pb isotope compositions of clean sulphide separates from the unmetamorphosed NA VMS deposits show limited variations and overlap the field of typical MORB basalts (Meyzen *et al.,* 2007) and of the least radiogenic metabasalts from the PZ ophiolites (Curti, 1987) (Fig. 5). The clear

MORB signature reflects the genesis of these deposits in seafloor and subseafloor, mafic- or ultramafic-hosted hydrothermal systems and a lack of significant contribution from oceanic sediments and continental sources (Fig. 6). This is consistent with the absence of sediments in the original oceanic substrate of the deposits (Ferrario & Garuti, 1980). No systematic differences in Pb isotope compositions are observed between deposits hosted in the External and Internal Ligurides (Table S1).

The variable shift of our *unrefined*, gangue-bearing samples towards higher $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios (Fig. 3) indicates the distinct isotopic signature of the primary sulphides relative to their host-rock minerals. The enrichment in ^{207}Pb and ^{208}Pb relative to ^{206}Pb in the silicate gangue suggests variable Pb contribution from continent-sourced oceanic sediments containing an old (model age ca. 500 Ma based on the ‘young upper crust’ model of Kramers & Toltsikhin, 1997) crustal Pb component. This Pb component would be isotopically similar to that contained in some pre-Alpine granitoids and metasediments from the Adria plate-related marginal units, which are now exposed in the western Southern Alps (feldspar data in Cumming *et al.,* 1987; Fig. 3). These units escaped Alpine metamorphism and may have been a source of continental detritus that accumulated in the Jurassic oceanic basin above the ore-bearing units. The observed variable enrichment in $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ is similar to, although much less extensive than, that reported for many Besshi-type VMS deposits and massive sulphides from present-day, sediment-covered mid-ocean ridges and ascribed to Pb leaching from mixed volcanic and sedimentary substrate rocks (*e.g.*, Cousens *et al.,* 2002). The absence of sediments in the footwall of the studied deposits (Ferrario & Garuti, 1980), however, suggests that in our case the enrichment is related to post-depositional processes, possibly connected with downward circulation of oceanic waters after burial beneath pelagic sediments (Fig. 6). Booij *et al.* (2000) described similar processes of post-depositional modification of the Pb isotope compositions in sulphide host-rocks, *without* concurrent isotopic modification of the sulphides included within them, in VMS deposits from the Troodos ophiolite complex, Cyprus. Possible clues of such post-depositional processes have been documented in several NA VMS deposits by Garuti & Zaccarini (2005), who found evidence of remobilisation of Au, Ag and Sn during seafloor weathering and, probably, early diagenesis, prior to or shortly after burial of the deposits under the volcanic or sedimentary cover. We suggest that during diagenesis, sediments accumulated above the sulphide-bearing units and rich in continent-derived materials released Pb to percolating chlorinated seawater. The mobilised Pb was then preferentially fixed on the gangue minerals of the sulphide deposits, possibly by sorption on phyllosilicates produced by hydrothermal alteration. Owing to the very low Pb contents in the original sulphide-bearing oceanic basalts and serpentinites, the uptake of a small fraction of continent-derived Pb could strongly modify the Pb isotope signature of the gangue. In turn, the very low Pb contents in the sulphides (mostly up to a few tens ppm; Garuti *et al.,* 2011; Table S2) allowed such modification to be detected in our unrefined, gangue-bearing samples.

Further occasional analyses departing off the MORB field towards higher ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb or ^{206}Pb/^{204}Pb ratios were previously reported for some ophiolite-hosted VMS deposits from the NA (OXALID, http://oxalid.arch.ox.ac.uk, accessed July 2015; Artioli *et al.,* 2009). As mentioned above, some of these data undoubtedly refer to secondary Cu minerals (Artioli *et al.,* 2009), which may have incorporated young radiogenic Pb from circulating groundwaters. Similar enrichments in radiogenic Pb of secondary Cu minerals were documented by Huelga-Suarez *et al*. (2014) and Artioli *et al*. (2016). Unfortunately, the OXALID data were not accompanied by detailed descriptions of the samples. Based on the systematics observed in our samples, we suspect that all anomalous, ^{207}Pb/^{204}Pb-enriched analyses reported in the literature for the NA VMS deposits reflect unrefined sample materials contaminated by Pb-bearing gangue minerals or by secondary products and may not be truly representative of the original hydrothermal sulphide compositions. For this reason, we will not consider these anomalous data any further.

5.2 Isotopic evolution during Alpine metamorphism

The uniform, non-radiogenic Pb isotope composition of the unmetamorphosed VMS deposits associated with the NA ophiolites and the two distinct trends observed for blueschist-facies and, respectively, eclogite-facies VMS deposits of the PZ (Fig. 2) suggest a major role of Alpine metamorphism and related fluids in the evolution of the Pb isotope signatures of the sulphides. Although within-deposit variations in the metamorphosed VMS deposits are sometimes significant, within each isotopic group no systematic variation is observed between pyrite-rich, chalcopyrite-rich and bornite-rich samples (Table S1). This is in line with what reported in modern seafloor VMS deposits, in which different sulphide minerals typically have similar Pb isotope compositions (*e.g.*, Fouquet & Marcoux, 1995; Andrieu *et al.,* 1998; Chernyshev *et al.,* 2011). Therefore, the observed Pb isotope trends are unlikely to be related to isotope fractionation between ore minerals during metamorphism. The overall Pb isotope pattern can rather be described in terms of mixing of at least three distinct Pb components, namely an original MORB component and two variously radiogenic continental components (Fig. 5). The distribution and possible origin of these continental components are discussed in detail below.

5.2.1 The old continental Pb component

The ^{207}Pb-enriched composition of the eclogite-facies VMS deposits relative to MORB Pb indicates incorporation of a relatively unradiogenic continental component, which could be isotopically similar to that contained in the feldspars of some *pre-Alpine* granitoids and metasediments from the Adria plate-related marginal units of the western Southern Alps (Cumming *et al.,* 1987) and in the gangue of the *unmetamorphosed* NA sulphides (*cf*. Fig. 3 and 5). The apparent absence of sediment intercalations in the original oceanic substrate of most of the studied eclogite-facies VMS deposits (see Supplementary Appendix) excludes a primary origin for their ‘continental’ isotopic signature. The restriction of the old continental Pb component to the eclogite-facies VMS deposits (Fig. 5) also suggests that this component could efficiently be mobilised and incorporated in the sulphides during eclogite-facies metamorphism, but not under less severe, blueschist-facies conditions. This can be explained considering the different affinity of metamorphic minerals for Pb. During subduction metamorphism, the ^{207}Pb-rich lead contained in the overlying sediments or in the sulphide gangue would probably first be redistributed to prograde lawsonite, epidote or titanite, which are the main Pb carriers in high-pressure, low-temperature metamorphic rocks (Spandler *et al.,* 2003; Martin *et al.,* 2014), and then be released to dehydration fluids upon their breakdown at the blueschist-to-eclogite transition (*cf.* Peacock, 1993). Petrographic evidence indicates that conditions for lawsonite and epidote breakdown were indeed exceeded in the eclogite-facies VMS host-rocks (Martin *et al.,* 2008; Rebay & Powell, 2012), but not in the blueschist-facies VMS host-rocks (Giacometti & Rebay, 2013). Also, Pb-poor rutile, rather than Pb-bearing titanite, became the typical stable Ti mineral at peak eclogitic conditions (*e.g.*, Martin *et al.,* 2008; Rebay & Powell, 2012), which could also contribute to release Pb. Even limited length-scale circulation of the dehydration fluids produced by eclogite-facies metamorphism would then allow redistribution of the ^{207}Pb-rich lead and its incorporation into the re-crystallising sulphides (Fig. 6). Given the small Pb contents in the original sulphides (*cf.* Garuti *et al.,* 2011, and Table S2), a small uptake of ^{207}Pb-rich lead could cause significant modification of their ^{207}Pb/^{204}Pb ratios and, eventually, obliteration of their original MORB signature.

It is noted that the isotopic composition of the eclogite-facies VMS deposits is also broadly similar to that of the HCl-leachate of one of the greenschist-facies retrogressed eclogites from the PZ analysed by Curti (1987) (Fig. 5). Like the sulphides, this rock may have interacted with fluids containing ^{207}Pb-rich lead released during eclogitic metamorphism of surrounding sediments; alternatively, it may have incorporated ^{207}Pb-rich lead at an earlier alteration stage by a process similar to that recorded in the gangue of the NA sulphides. Unfortunately, a detailed mineralogical description of this sample was not provided, therefore the significance of its HCl-leachate remains unclear.

5.2.2 The young continental Pb component

The well-defined isotopic trend shown by the blueschist-facies VMS deposits can be interpreted as the result of mixing of an original MORB Pb with a relatively radiogenic continental Pb component (Fig. 5). Potential sources of this component are continental rocks from European plate-related, inner-Penninic units *that were subjected to Alpine metamorphism*, such as the metagranites and metapelites from the M. Rosa nappe analysed by Curti (1987). Mineral separates, whole-rocks and HCl-leachates from these sources are, on average, distinctly more radiogenic than feldspars from the western Adria basement rocks that, instead, escaped Alpine metamorphism (Fig. 5). Unfortunately, Pb isotope data for the calcschists, the main lithology in the blueschist-facies PZ, are restricted to two whole-rock samples from the Brusson area (Combin Zone) studied by Pettke & Diamond (1997). Their $^{207}Pb/^{204}Pb$ ratios are too low to account for the continental Pb contained in the most radiogenic VMS deposits (Fig. 5). The shift of these two calcschists towards more mantle-like compositions relative to the continental inner-Penninic units suggests that their sedimentary protoliths had incorporated a minor contribution of MORB Pb derived from oceanic crustal rocks along with their dominant continent-sourced detrital Pb. However, a derivation of continental Pb with higher $^{207}Pb/^{204}Pb$ from calcschists devoid of oceanic crust-sourced material cannot be excluded.

The presence of the young continental Pb component in the eclogite-facies VMS deposits is uncertain (Fig. 5), although within-deposit isotopic variations may suggest mixing of variably radiogenic crustal components (Fig. 2). A young continental Pb component is significant or even dominant, however, in some greenschist-facies, retrogressed eclogites from the PZ and in a synmetamorphic feldspar pod contained within them (Curti, 1987; Fig. 5); according to Curti (1987), the former were variously contaminated by continental components, whereas the latter was segregated from fluids derived from neighbouring continental units. The presence of the young continental component in both blueschist-facies VMS deposits and greenschist-facies, retrogressed eclogites, suggests an origin from circulation of metamorphic fluids released during the greenschist-facies metamorphism, which variably overprinted both the eclogite-facies and the blueschist-facies units. Circulation of such fluids is believed to be normally restricted to local rocks, unless focused along favourable tectonic structures (Henry *et al.,* 1996; Agard *et al.,* 2000). On this basis, the continental Penninic units that tectonically underlie the PZ (*e.g.*, the M. Rosa nappe) would not be the best candidate Pb sources, despite their compatible isotopic compositions. Rather, PZ calcschist units rich in continent-sourced detrital Pb can be considered as the most likely source of radiogenic continental Pb in the associated VMS deposits (Fig. 6). The general scarcity of terrigenous metasediments in the eclogitic units may have limited the availability of this Pb to the eclogite-facies VMS deposits.

5.3 Lead in post-collision hydrothermal veins

5.3.1 Veins in eclogitic units

The isotopic similarity between the post-collision hydrothermal veins in the eclogitic-facies PZ and the VMS deposits that contain the highest proportion of continental Pb components (Fig. 4) indicates the presence of similar components also in the veins. As in the case of the VMS deposits, PZ calcschists may be good candidate sources of the more radiogenic component, whereas remobilisation of Pb contained in eclogite-facies, ophiolite-hosted sulphides may have supplied the less radiogenic component (Fig. 6). The strong Ni–Co specialisation of the Cruvino and Usseglio deposits (Table S2) also suggests a geochemical relationship with the (ultra)mafic rocks of the host ophiolitic complex, which could be a rich source of these elements (*cf.* Herrington *et al.,* 2005; Melekestseva *et al.,* 2013, 2017). However, the potential involvement of tectono-stratigraphically lower Penninic units as metal sources is difficult to exclude, as the post-collision veins may have collected far-travelled fluids that migrated along ductile to brittle shear zones or other tectonic pathways (*cf.* Bistacchi *et al.,* 2001) (Fig. 6). The isotopic similarity and partial mineralogical affinity of the La Reale deposit (^{206}Pb/^{204}Pb = 18.718–18.756, ^{207}Pb/^{204}Pb = 15.631–15.665, ^{208}Pb/^{204}Pb = 38.692–38.747; Table S1), an Au-rich, polymetallic quartz vein, with the widespread mesothermal gold lodes of the M. Rosa Gold District ($^{206}Pb/^{204}Pb$ = 18.674–18.802, $^{207}Pb/^{204}Pb$ = 15.649–15.691, $^{208}Pb/^{204}Pb$ = 38.635–38.848, for the final sulphide-rich stage; Curti, 1987; Pettke & Frei, 1996), interpreted to contain a mixture of metals derived from deep PZ and inner-Penninic continental units (Pettke & Diamond, 1997; Pettke *et al.,* 1999, 2000), is consistent with the far-travelled-fluid hypothesis.

5.3.2 The blueschist-hosted Saint-Véran deposit

The Saint-Véran synmetamorphic vein is peculiar for its geological, mineralogical and geochemical features and for its very wide isotopic variability (Fig. 4). The synkinematic nature of the mineralisation and the presence of late porphyroblastic albite in the pre-ore assemblage (Routhier, 1946; Tuduri, 2001) suggest that the hydrothermal deposition developed during exhumation of the host calcschists after the high-pressure (lawsonite–glaucophane) metamorphism. The Na-rich silicate matrix and diffuse albitisation in economic and barren sectors of the ore-bearing structure (Routhier, 1946; Tuduri, 2001) also indicate that sulphide deposition was preceded by infiltration of sodic metasomatic fluids. The Saint-Véran deposit evidently contains a non-equilibrium mixture of Pb derived from different sources. The analysed bornite-rich samples are, on average, the least radiogenic and contain significant Zn, Ag, Te, Ni and Co, with Ni/Co > 1 (Table S2). The low $^{207}Pb/^{204}Pb$ ratio of some of these samples and the high Ni (Co) contents indicate the presence of a significant, mantle-related (ultra)mafic component (Kramers & Toltsikhin, 1997; Melekesteva *et al.,* 2013, 2017). Such component could be derived either from adjacent chlorite schists and talc schists or from deeper ophiolitic bodies. Extensive reaction of a metamorphic fluid with ultramafic wall-rocks has been proposed to drive the fluid towards sodic alkaline compositions (Albino, 1995), thus providing a potential genetic link between the documented sodic metasomatism and the external supply of mantle Pb from ophiolitic ultramafic rocks. It is worth noting that the sample with the highest $^{207}Pb/^{204}Pb$ ratio and thus strongest continental signature also has the highest Pb content (2400 ppm; Table S1 and S2), whereas the sample with the lowest $^{207}Pb/^{204}Pb$ ratio and more MORB-like isotopic signature contains the highest proportion of sphalerite (Table S1 and Fig. S1h). These systematics support mixing of distinct leads with MORB and continental affinity, respectively, with increasing proportion of the latter in the Pb-rich and sphalerite-poor mineral assemblages.

Following our interpretation of the origin of old continental Pb in the eclogite-facies VMS deposits (see section 5.2.1), the high-$^{207}Pb/^{204}Pb$ component in Saint-Véran bornites may have been released by deeper units undergoing prograde eclogite-facies metamorphism or by remobilisation of sulphides contained in deeper eclogite-facies ophiolitic units (Fig. 6). The Saint-Véran chalcopyrite samples instead have an isotopic composition more similar to those of several blueschist-facies VMS deposits of the PZ (Fig. 4). By analogy with these VMS deposits (see section 5.2.2), we interpret the compositions of these chalcopyrites to reflect a mixture of ophiolite-sourced, MORB Pb and host calcschist-sourced, young 'continental' Pb.

We note that our interpretation of the Saint-Véran deposit is in contrast with that of Bouladon & Picot (1968), Ayoub (1984) and Bouvier *et al. (*1990), who proposed a seafloor hydrothermal origin as a massive sulphide deposit, followed by intense metamorphic remobilisation. We believe that our scenario provides a better interpretation for the presence of unusual ore-bearing riebeckite-rich (up to ca. 90%) rocks, whose composition would be difficult to ascribe to reasonable seafloor protoliths, for the substantial rarity of Fe sulphides, which are the main constituents in typical VMS deposits regardless of metamorphism, and for the presence of an 'eclogitic' Pb trait in an ore deposit that never experienced eclogite-facies conditions.

5.4 Mobility of subducted oceanic Pb

Our interpretation of Pb isotope systematics in PZ VMS deposits implies that (i) small-scale circulation of Pb-bearing metamorphic fluids is sufficient to explain the isotopic evolution of the sulphides during subduction up to eclogite-facies conditions (ca. 530–600 °C and ≥2.1 GPa for the Zermatt–Saas units; Bucher *et al.,* 2005; Martin *et al.,* 2008; Angiboust *et al.,* 2009; Groppo *et al.,* 2009; Rebay & Powell, 2012) and that (ii) during this evolution the sulphides acted as a sink rather than a source of Pb. Therefore, release of sulphide-hosted Pb, and by inference of other sulphide-hosted metals, during prograde metamorphism of the now exposed sectors of the subducted oceanic crust was negligible. This is consistent with independent evidence for a scarce mobility of sulphur during high-pressure metamorphism in sulphide deposits from the same area (Dale *et al.,* 2009; Giacometti *et al.,* 2014) and for preservation of primary sulphides in high-pressure metamorphic rocks from the same area up to 600 °C and from other mountain belts up to 750 °C (Tomkins & Evans, 2015).

When combined with independent evidence for negligible release of Pb from metabasites during metamorphism to 1.6–1.9 GPa and 550–620 °C (Spandler *et al.,* 2003), our data suggest a limited mobility of subducted oceanic Pb up to eclogite-facies conditions. This does not exclude that oceanic units metamorphosed under more severe conditions could release part of their Pb to devolatilisation fluids. Release of Pb from unexposed, higher-grade ophiolitic units has indeed been proposed for fluids responsible for the formation of Cenozoic mesothermal gold lodes in the north-western Alps (Monte Rosa Gold District) (Pettke & Diamond, 1997; Pettke *et al.,* 1999, 2000) and for some high-grade amphibolites (up to 850 °C) from the Franciscan subduction complex and Feather River ultramafic belt, California (Ghatak *et al.,* 2012), and could explain the presence of 'eclogitic' isotopic traits in the blueschist-hosted, post-collision Saint-Véran vein deposit (see section 5.3.2).

6. Concluding remarks

Owing to their relatively low Pb grades, seafloor hydrothermal massive sulphides deposits from the ophiolite-bearing PZ can serve as sensitive monitors of Pb mobility during the Alpine orogenic cycle and subduction- and collision-related metamorphism. The main implications of the isotopic study of these sulphides can be summarised as follows.

(1) Sulphides metamorphosed under eclogite-facies conditions are isotopically distinct from those metamorphosed under blueschist-facies conditions and from those that escaped Alpine metamorphism.

(2) The ^{207}Pb-enriched isotope composition of the eclogite-facies sulphides reflects uptake during prograde metamorphism of an old continental Pb component, which was originally contained in gangue minerals or in neighbouring oceanic sediments.

(3) The blueschist-facies sulphides recorded mixing of seafloor-inherited MORB Pb with young continental Pb, which was probably released by neighbouring calcschists during collision-related greenschist-facies metamorphism.

(4) Release of sulphide-hosted Pb, and by inference of other sulphide-hosted metals, during prograde metamorphism of presently exposed ophiolitic units appears to have been negligible.

(5) Mobilisation of Pb from both ophiolitic and deeper continental units occurred during or after collisional metamorphism by local-scale pervasive or larger-scale focused circulation of metamorphic fluids, and produced polymetallic sulphide veins containing variable proportions of MORB and continental Pb.

Acknowledgements: We are grateful to I. Villa for his help during isotopic analyses and to G.V. Dal Piaz for reviewing an early version of the manuscript and for his precious suggestions. Constructive reviews by J.S. Daly and an anonymous referee helped us improve the paper. J. Tuduri is thanked for useful discussion on the Saint-Véran deposit. We are also thankful to P. Rostan and M. Scacchetti for their help during field sampling of the Saint-Véran and Apenninic deposits. PN acknowledges financial support by Progetto di Ateneo 2013 CPDA138741 ‘‘Copper metallogenesis and provenancing in the Alpine realm” (University of Padua).

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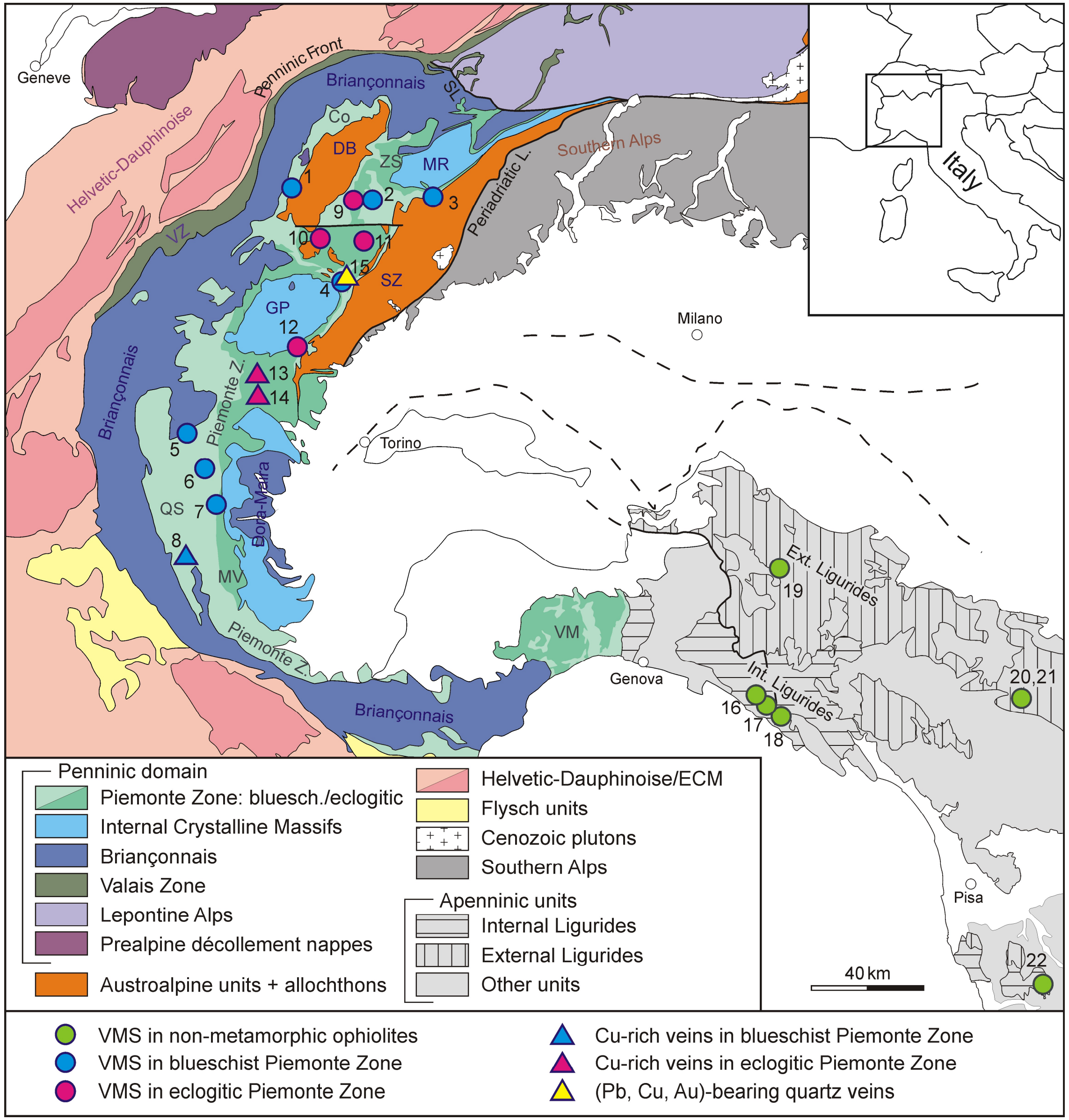
Geneve
Penninic Front
Briançonnais
SL
Helvetic-Dauphinoise
Co
DB
ZS
MR
Southern Alps
Periadriatic L.
VZ
1
2
3
9
10
11
15
4
SZ
GP
12
Milano
13
14
Piemonte Z.
Briançonnais
5
Torino
6
QS
7
Dora-Maira
8
MV
Ext. Ligurides
19
VM
Piemonte Z.
Genova
Int. Ligurides
20,21
16
17
18
Briançonnais
Italy
Pisa
22
40 km
Penninic domain
Piemonte Zone: bluesch./eclogitic
Internal Crystalline Massifs
Briançonnais
Valais Zone
Lepontine Alps
Prealpine décollement nappes
Austroalpine units + allochthons
Helvetic-Dauphinoise/ECM
Flysch units
Cenozoic plutons
Southern Alps
Apenninic units
Internal Ligurides
External Ligurides
Other units
VMS in non-metamorphic ophiolites
VMS in blueschist Piemonte Zone
VMS in eclogitic Piemonte Zone
Cu-rich veins in blueschist Piemonte Zone
Cu-rich veins in eclogitic Piemonte Zone
(Pb, Cu, Au)-bearing quartz veins

Fig. 1. Tectonic map of the Western Alps and Northern Apennines (adapted from Bigi *et al.,* 1990, Beltrando *et al.,* 2014, and Carmignani *et al.,* 2012) and location of deposits studied (numbers as in Table 1). Co: Combin Zone; DB: Dent Blanche nappe; ECM: External Crystalline Massifs; GP: Gran Paradiso massif; MV: Monviso massif; MR: M. Rosa massif; QS: Queyras Schistes Lustrés; SL: Sempione Line; SZ: Sesia Zone; VM: Voltri massif; VZ: Valais Zone; ZS: Zermatt-Saas Zone.

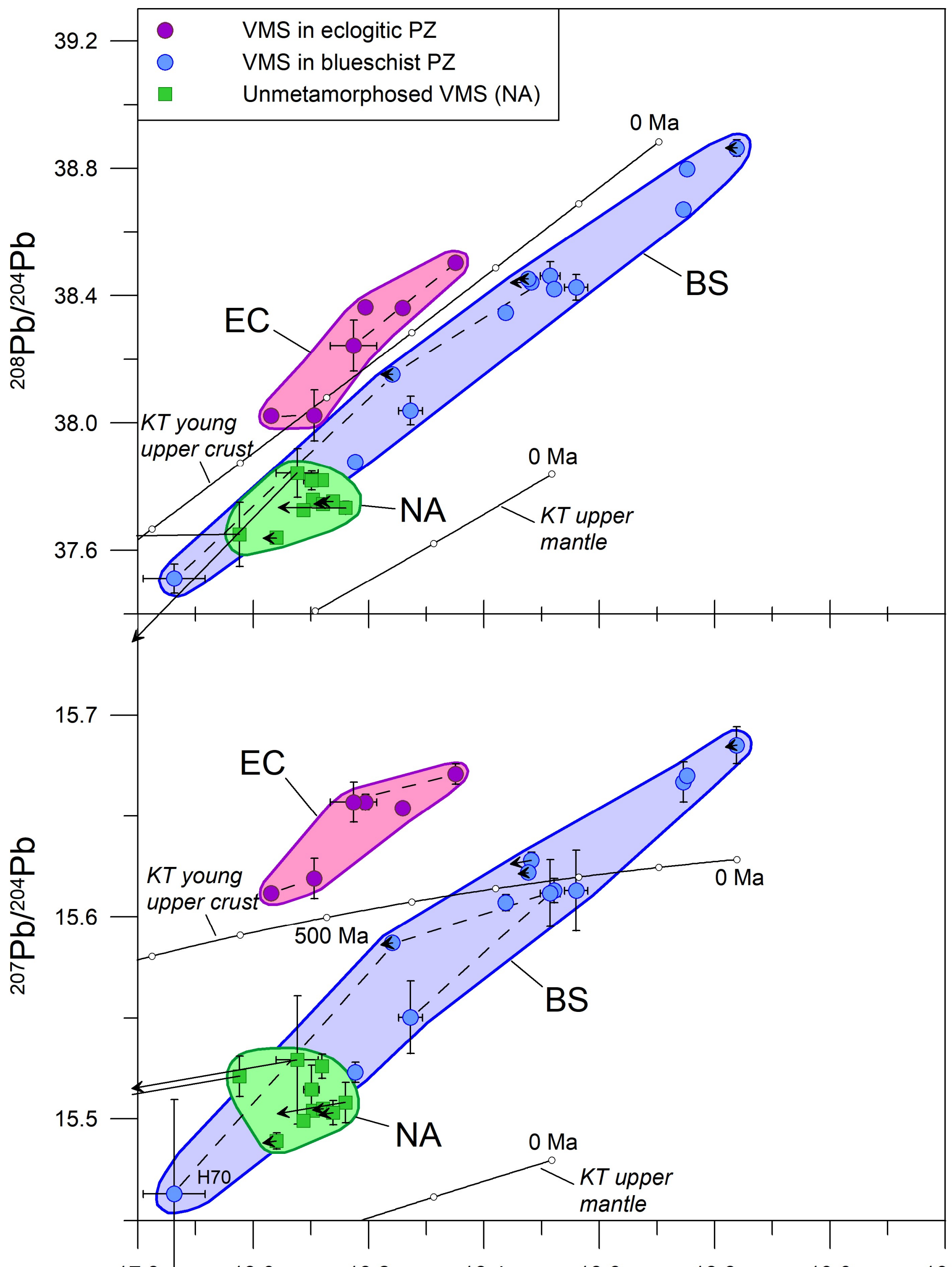
● VMS in eclogitic PZ
● VMS in blueschist PZ
🟩 Unmetamorphosed VMS (NA)
39.2
38.8
38.4
38.0
37.6
^{208}Pb/^{204}Pb
0 Ma
EC
BS
KT young upper crust
0 Ma
NA
KT upper mantle
15.7
15.6
15.5
^{207}Pb/^{204}Pb
EC
KT young upper crust
500 Ma
0 Ma
BS
NA
0 Ma
H70
KT upper mantle

Fig. 2. Lead isotope ratios of VMS deposits in non-metamorphic units from NA and in eclogite-facies (EC) and blueschist-facies (BS) units from PZ. Sample H70 from Alagna deposit after Curti (1987). Dashed lines connect samples from the same deposit. Symbols indicate uncorrected data. Arrows connect uncorrected data with age-corrected data at 170 Ma (*i.e.*, the maximum reported age for the oceanic stage) for the same samples (not shown if smaller than symbol). Note that this age may significantly overestimate the time of last isotopic closure for the metamorphosed deposits. One of the NA samples showed unrealistically low corrected ratios falling well off the limits of the plot (truncated arrow). KT: Pb growth curves after Kramers & Toltsikhin (1997), with reference marks at 100-My intervals. Error bars (2σ) not shown when smaller than symbol.

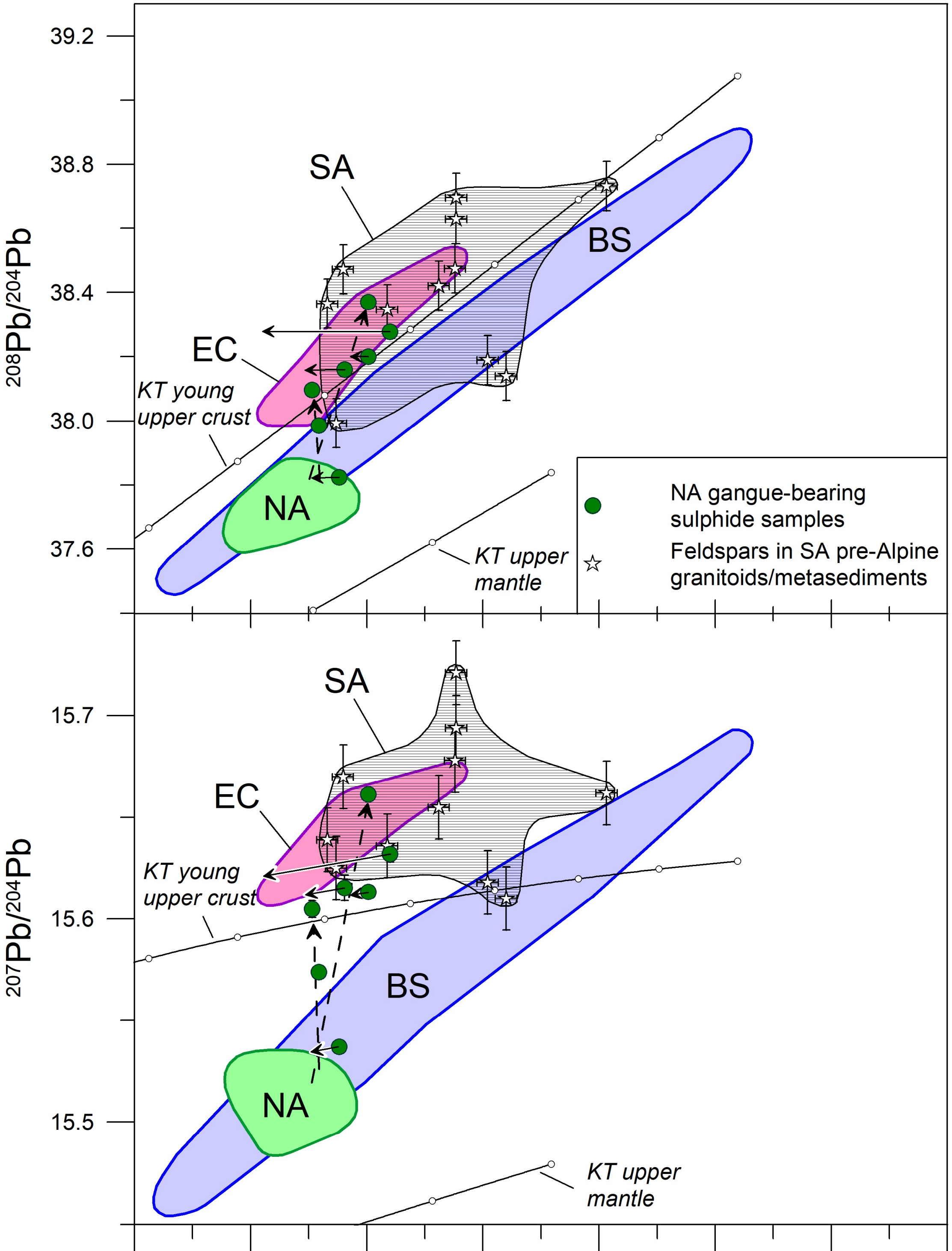
^{208}Pb/^{204}Pb
39.2
38.8
38.4
38.0
37.6
SA
BS
EC
KT young upper crust
NA
KT upper mantle
● NA gangue-bearing sulphide samples
☆ Feldspars in SA pre-Alpine granitoids/metasediments
^{207}Pb/^{204}Pb
15.7
15.6
15.5
SA
EC
KT young upper crust
BS
NA
KT upper mantle

Fig. 3. Lead isotope ratios for gangue-bearing samples of unmetamorphosed VMS deposits from the NA. Dashed arrows show the shift with respect to clean sulphide separates from the same samples (*cf.* Fig. 2). The data indicate mixing of sulphide-borne low-$^{207}Pb/^{204}Pb$ lead and gangue-borne high-$^{207}Pb/^{204}Pb$ lead. Feldspar data for pre-Alpine granitoids and metasediments from the western Southern Alps (SA, gray shaded field) after Cumming *et al.* (1987) are shown for comparison. Solid arrows show the effect of age correction (close system) at 170 Ma (*i.e.*, the maximum reported age for the oceanic stage) for NA samples (not shown if smaller than symbol). Feldspar data do not require age correction, due to the low U/Pb and Th/Pb ratios typical for these minerals. Error bars (2σ) not shown when smaller than symbol. All other reference fields and curves as in Fig. 2.

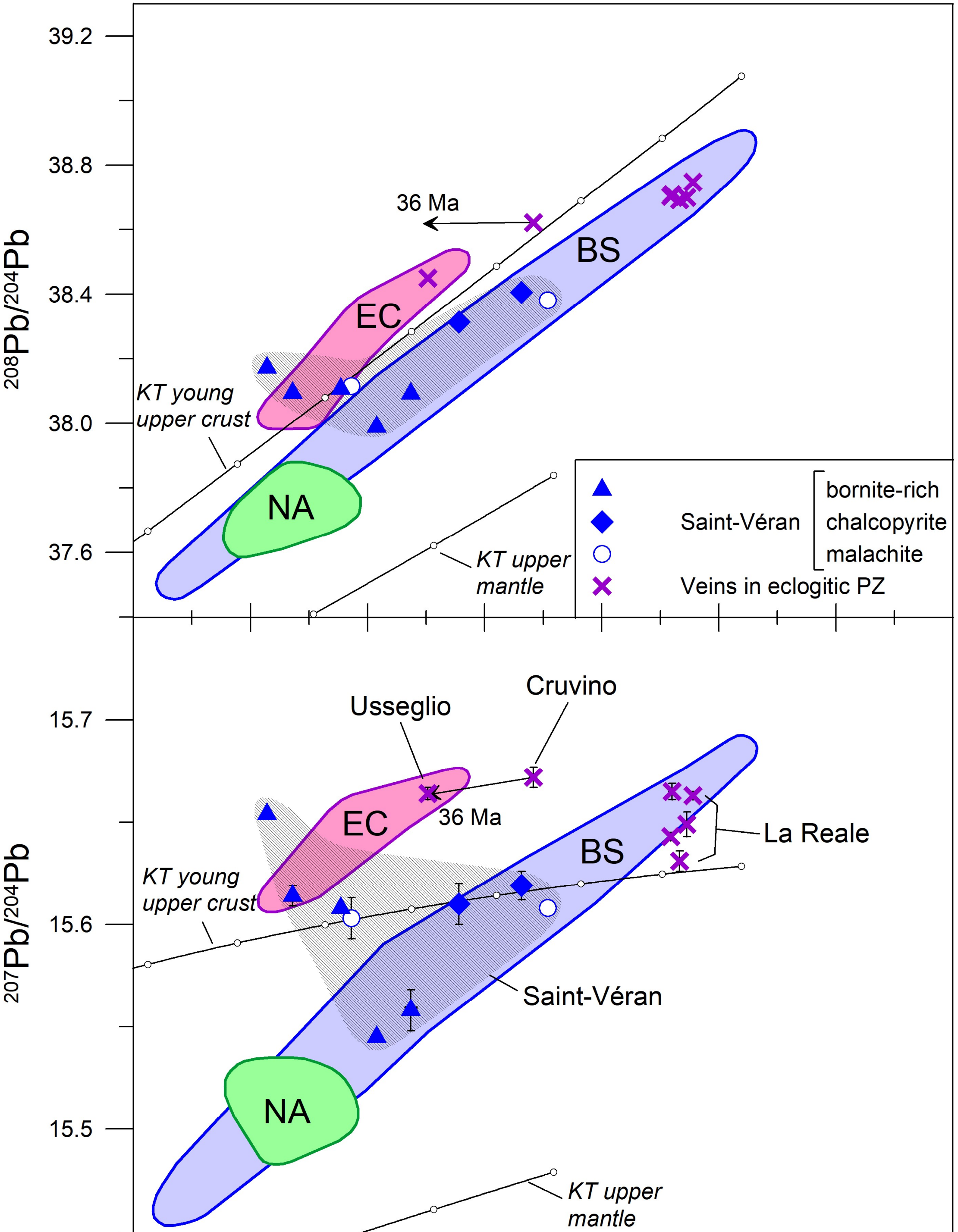
39.2
38.8
38.4
38.0
37.6
^{208}Pb/^{204}Pb
36 Ma
BS
EC
NA
KT young upper crust
KT upper mantle
▲
◆
○
×
Saint-Véran
bornite-rich
chalcopyrite
malachite
Veins in eclogitic PZ
15.7
15.6
15.5
^{207}Pb/^{204}Pb
Usseglio
Cruvino
36 Ma
EC
BS
La Reale
KT young upper crust
Saint-Véran
NA
KT upper mantle

Fig. 4. Lead isotope ratios for syn-metamorphic (Saint-Véran, gray shaded field) and post-metamorphic (Usseglio, Cruvino, La Reale) vein deposits in the PZ. Arrow shows the relatively large effect of age correction for one of the veins in the eclogitic PZ (Cruvino) at the maximum age for greenschist-facies metamorphism (36 Ma), which should be considered as a maximum correction. Age correction could not be performed for the well-clustered La Reale samples, for which trace element data are not available, but is assumed to be negligible given the presence of very Pb-rich and U-Th-poor galena in most of them. Age correction for all other samples had negligible effects (Table S1). Error bars (2σ) not shown when smaller than symbol. All other reference fields and curves as in Fig. 2.

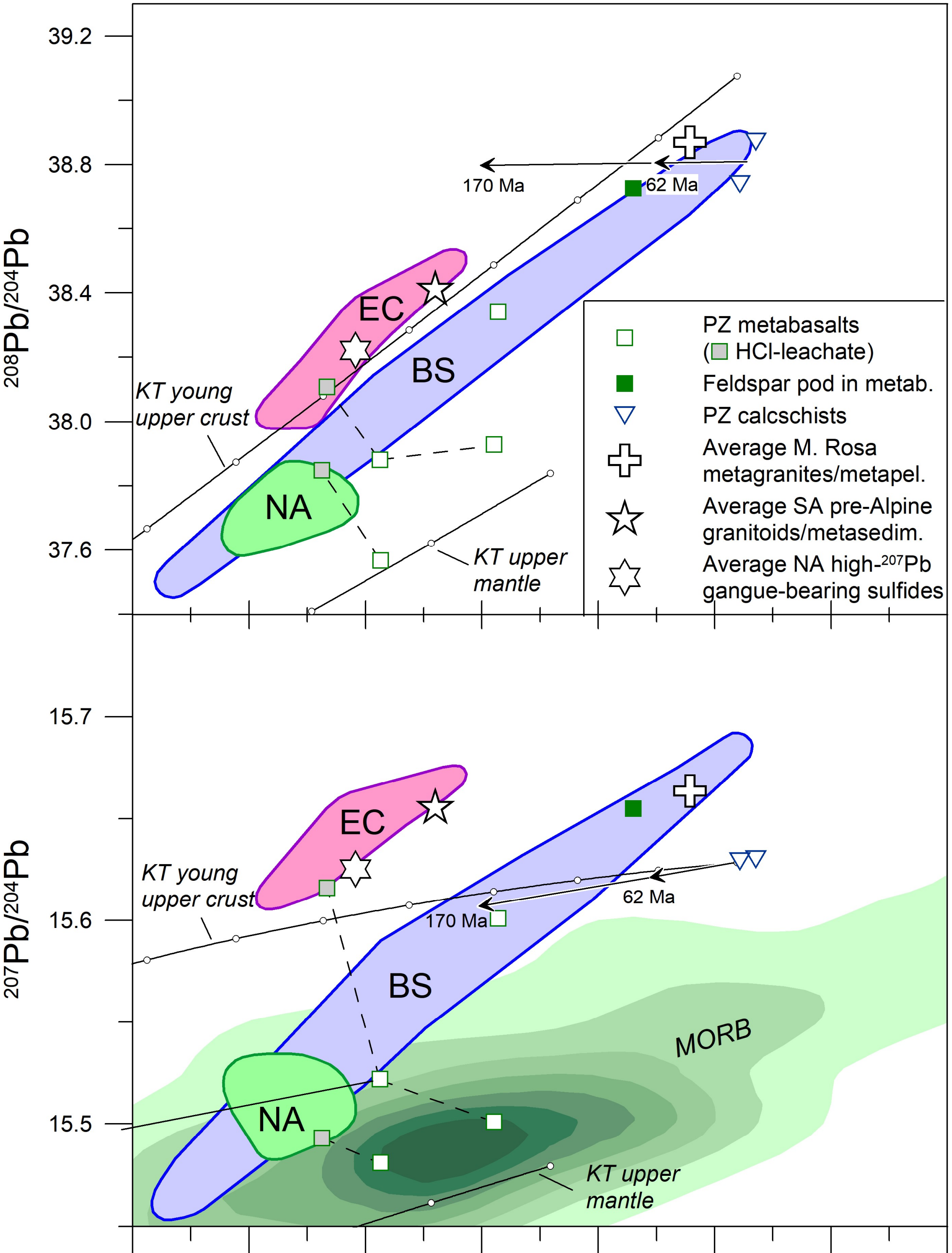
39.2
38.8
38.4
38.0
37.6
^{208}Pb/^{204}Pb
170 Ma
62 Ma
EC
BS
NA
KT young upper crust
KT upper mantle
PZ metabasalts
(▨ HCl-leachate)
Feldspar pod in metab.
PZ calcschists
Average M. Rosa metagranites/metapel.
Average SA pre-Alpine granitoids/metasedim.
Average NA high-^{207}Pb gangue-bearing sulfides
15.7
15.6
15.5
^{207}Pb/^{204}Pb
EC
KT young upper crust
62 Ma
170 Ma
BS
MORB
NA
KT upper mantle

Fig. 5. Comparison between the studied VMS deposits (EC, BS and NA fields as in Fig. 2) and potential Pb reservoirs, represented by MORB basalts (MC-ICP-MS data from various sources as compiled in Meyzen *et al.,* 2007, contoured at kernel densities of 1 to 15), and by average compositions of (i) metagranites and metapelites from M. Rosa nappe (mostly feldspar data; Curti, 1987), (ii) pre-Alpine granitoids and metasediments from the western Southern Alps (feldspar data; Cumming *et al*., 1987), and (iii) the five gangue-bearing sulphide samples with the highest ^{207}Pb/^{204}Pb ratios from NA (*cf*. Fig. 4). Existing data for PZ calcschists (whole-rock data; Pettke & Diamond, 1997), metabasalts and metabasalt-hosted synmetamorphic feldspar pods (feldspar, clinozoisite, whole-rock and HCl-leached whole-rock data; Curti, 1987) are also shown for comparison. Dashed lines connect data referring to the same sample. In the upper plot, data for MORB (not shown for clarity) are highly scattered and mostly fall between the upper mantle and young upper crust curves. Arrows indicate effect of age correction (closed system) for the calcschists at 62 Ma (*i.e.*, maximum age of high-P metamorphism) and 170 Ma (*i.e.*, maximum pre-metamorphic depositional age). Age correction for one whole-rock metabasalt (truncated solid line) produced unrealistically low isotope ratios, plotting far outside the plot limits. Feldspar and clinozoisite data do not require age correction, due to the low U/Pb and Th/Pb ratios typical for these minerals. Age-correction for NA gangue-bearing samples at the age of eclogitic metamorphism has negligible effects. Reference curves as in Fig. 2.

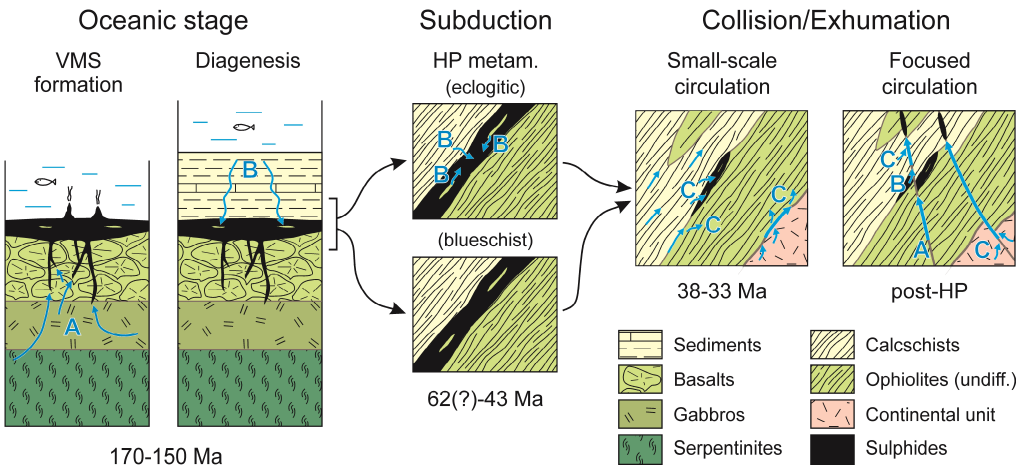

Fig. 6. Schematic scenario for the circulation of fluids and Pb isotopic components, from ocean spreading through Alpine orogeny. *Oceanic stage*: circulation of seawater through the oceanic crust leads to formation on seafloor of VMS deposits containing a MORB-like Pb-component (A); during diagenesis, a second Pb-component (B) is leached by percolating seawater from sediments containing continent-derived detritus and is fixed on the sulphide gangue minerals. *Subduction*: sediments and gangue minerals undergoing eclogite-facies metamorphism release Pb-component B, which is incorporated into the re-crystallising sulphides. *Collision/Exhumation*: small-scale fluid circulation during greenschist-facies metamorphism mobilises a more radiogenic Pb-component (C) from calcschists and continental basement units that had already experienced Alpine metamorphism; this Pb component is then incorporated in sulphides and some retrogressed metabasites. Focused circulation of fluids during or after Alpine metamorphism leads to formation of polymetallic sulphide veins containing variable proportions of both locally-derived and long-travelled Pb components.

Table 1. Main features and geological setting of the deposits studied.

Deposit	**Host unit**	**Deposit type**	**Main minerals**†	**References**
1. Ollomont	Blueschist-facies Piemonte Zone	VMS (massive stratiform)	py >> ccp (tr. sp)	Dal Piaz & Omenetto (1978)
2. Mont Ros (V. d'Ayas)	Blueschist-facies Piemonte Zone	VMS (massive stratiform)	py >> ccp (tr. sp)	Dal Piaz & Omenetto (1978)
3. Alagna, Fabbriche	Blueschist-facies Piemonte Zone	VMS (massive stratiform)	py >> ccp (po, mag, sp)	Dal Piaz & Omenetto (1966)
4. Colle della Borra	Blueschist-facies Piemonte Zone	VMS (massive with remobilisation)	py >> ccp (sp)	Benciolini *et al*. (1984)
5. Salbertrand	Blueschist-facies Piemonte Zone	VMS (massive stratiform)	py >> ccp (tr. sp)	Natale (1966)
6. Beth-Ghinivert	Blueschist-facies Piemonte Zone	VMS (massive stratiform)	py >> ccp (tr. sp, mag)	Natale & Visetti (1980)
7. Via Fiorcia	Blueschist-facies Piemonte Zone	VMS (massive stratiform)	ccp, bn, py, mag (cct, dg, cv, po, sp, lin, tnt)	Dal Piaz *et al*. (1978)
8. Saint-Véran–Les Clausis	Blueschist-facies Piemonte Zone	Metamorphogenic vein	bn, sp, cct, dg > ccp, py, hem (Te) in rbk, aeg, mag, qz	Routhier (1946)
9. Petit Monde	Eclogite-facies Piemonte Zone	VMS ? (with intense remobilisation)	py >> ccp (po, sp, bn)	Burtet-Fabris *et al*. (1971)
10. Chuc–Servette	Eclogite-facies Piemonte Zone	VMS (massive stratiform)	py >> ccp (sp, bn, po, cct, mrc, mk)	Martin *et al*. (2008)
11. Hérin	Eclogite-facies Piemonte Zone	VMS (massive stratiform)	py >> ccp (sp, mag, po)	Brigo *et al*. (1976)
12. Chialamberto, Fragnè	Eclogite-facies Piemonte Zone	VMS (massive stratiform)	py >> ccp (sp)	Zuccato (1970)
13. Usseglio	Eclogite-facies Piemonte Zone (metabasite)	Ni–Co–Cu–As (Sb) veins	Ni–Co–Fe arsenides, ttr, ccp, sp, py in sd, ank, qz, brt	Castelli *et al*. (2011)
14. Cruvino	Eclogite-facies Piemonte Zone (serpentinite, metabasite)	Ni–Co–Cu–As (Sb) veins	Ni–Co–Fe arsenides, ttr, apy, py in sd, cal, dol, qz	Fenoglio & Fornaseri (1940)
15. La Reale (Piamprato, Valprato Soana)	Eclogite-facies Piemonte Zone (calcschist)	Polymetallic Pb–Cu (Au) vein	py, po, gn, ccp (Au) in qz (sd)	This work
16. Libiola	Internal Liguride ophiolites (basalt)	VMS (massive stratabound)	py >> ccp (po, sp)	Zaccarini & Garuti (2008)
17. M. Loreto	Internal Liguride ophiolites (basalt)	VMS (massive stratabound)	py >> ccp (po, sp)	Ferrario & Garuti (1980)
18. Piazza	Internal Liguride ophiolites (gabbro)	VMS-related stockwork	py, ccp, sp	Ferrario & Garuti (1980)
19. Vigonzano, Cantiere Vaie	External Liguride ophiolites (serpentinite)	VMS-related stockwork	py > ccp > mag (sp, mrc, po) in qz, srp, tlc, cal (sap)	Zaccarini & Garuti (2008)
20. Boccassuolo, Miniera Labirintica	External Liguride ophiolites (basalt)	VMS-related stockwork	ccp, sp, py in qz (cal, chl, ep, ttn)	Zaccarini & Garuti (2008)
21. Boccassuolo, Filone Omar	External Liguride ophiolites (basalt)	VMS-related stockwork	sp, ccp in qz	Garuti *et al*. (2008)
22. Montecatini Val di Cecina	Internal Liguride ophiolites (basalt)	VMS-related stockwork	ccp, py (bn) (cct, bn in cementation zone)	Bertolani & Rivalenti (1973)

Notes:

[†] Based on listed references and own observations; aeg – aegirine, ank – ankerite, apy – arsenopyrite, brt – barite, bn – bornite, cal – calcite, cct – ‘chalcocites’, chl – chlorite, ccp – chalcopyrite, cv – covellite, dg – digenite, dol – dolomite, ep – epidote, gn – galena, hem – hematite, lin – linnaeite, mag – magnetite, mrc – marcasite, mk – mackinawite, po – pyrrhotite, py – pyrite, qz – quartz, rbk – riebeckite, sap – saponite, sch – scheelite, srp – serpentine, sd – siderite, sp – sphalerite, tlc – talc, tnt – tennantite, ttr – tetrahedrite, ttn – titanite.