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Ignimbrite correlation using whole-rock geochemistry: an example from the Sulcis (SW Sardinia, Italy)

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Abstract – Ignimbrites are useful chronological markers in the geological record at local and regional scales. They also provide information on the dynamics of the eruption that produced them, making their study of great importance in terms of volcanic hazard assessment. However, their study is usually hampered by their lateral variation and discontinuity. When stratigraphic and lithologic criteria are not sufficient for correlation purposes, the use of multiple complementary correlation tools may be necessary to correctly determine their areal extension, volume and facies variations. Whole-rock geochemistry is considered one of the less reliable correlation techniques due to the pyroclastic nature of these deposits and their emplacement dynamics. These may introduce vertical and horizontal geochemical heterogeneity in the final deposit. In addition, the occurrence of zoned ignimbrites due to magma supply of changing composition is common. In this work we show that, if appropriately used, whole-rock geochemistry can be a valid and highly useful tool for ignimbrite correlation. We provide an example from the study of an ignimbrite sequence containing 18 units (*sensu lato*) in the Sulcis region (SW Sardinia, Italy). A protocol has been developed for unit recognition based on successive simple binary diagrams where the whole-rock composition of a problem sample can be plotted. Immobile trace elements have been preferentially used to minimize effects of element mobilization associated with alteration and weathering. The diagrams provided here are designed for the Sulcis, but the methodology followed to develop them may be applied to other study areas.

Keywords: whole-rock geochemistry, ignimbrites, correlation, binary diagrams, Sardinia.

1. Introduction

Ignimbrites are deposits emplaced by pyroclastic density currents (PDC). They can vary from low-volume strongly topographically controlled finger-like deposits some hundreds of metres long, to large volume sheets that can cover areas up to several thousand square kilometres away from the eruptive vent (Branney & Kokelaar, 1992, 2002). Some of the biggest-known single ignimbrites are those of Toba and Yellowstone, which exceed 3000 km^3 (Wilson, 1993; Best *et al.* 2013). Large areal extents and instantaneous formation (in geological time) of voluminous ignimbrites turn these deposits into valuable chronological marker horizons at a local and regional scale (e.g. Glazner *et al.* 1986; McIntosh, 1991). Ignimbrites are also usually the only source of information on the PDC that generated them (Branney & Kokelaar, 1992, 2002), on the eruptions that originated those flows (e.g. Sumner & Wolff, 2003) and on the dynamics of the magma chamber (e.g. Sumner & Branney, 2002; Sumner & Wolff, 2003; Bachmann & Bergantz, 2008; Wolff & Ramos, 2014).

However, the study of ignimbrite deposits and their correlation throughout a study area may be problematic due to: (1) irregular areal distribution caused by topographically influenced channelized flow and deposition; (2) frequent detachment from the source of the PDC, which hampers the correlation of the deposits to their vent; (3) vertical and horizontal zonation in physical and chemical properties and clast distribution; and (4) erosional and tectonic processes that break the continuity of the ignimbrites after emplacement (Hildreth & Mahood, 1985; Branney & Kokelaar, 1992, 2002; Harangi, Mason & Lukacs, 2005; Bachmann & Bergantz, 2008).

When stratigraphy and lithology are not sufficient for deposit correlation, several complementary correlation tools can be used. The most common are: single glass shard geochemistry (e.g. Peate *et al.* 2003; Harangi, Mason & Lukacs, 2005; Suzuki *et al.* 2005; Pearce, Alloway & Westgate, 2008; Jutzeler, Schmincke & Sumita, 2010; Sumita & Schmincke, 2013); single pumice geochemistry or pumice/glass separate geochemistry (e.g. Lebti *et al.* 2006; Di Vito *et al.* 2008; Cassel, Calvert & Graham, 2009; Jutzeler, Schmincke & Sumita, 2010; Aydar *et al.* 2012); mineral chemistry (e.g. Shane, 1998; Harangi, Mason & Lukacs, 2005; Lebti *et al.* 2006; Jutzeler, Schmincke & Sumita, 2010; Aydar *et al.* 2012; Ellis *et al.* 2012; Sumita & Schmincke, 2013); $^{40}Ar/^{39}Ar$ dating (e.g. McIntosh, 1991; Lebti *et al.* 2006; Aydar *et al.* 2012; Ellis *et al.* 2012; Speranza, Di Chiara & Rotolo, 2012; Best *et al.* 2013);

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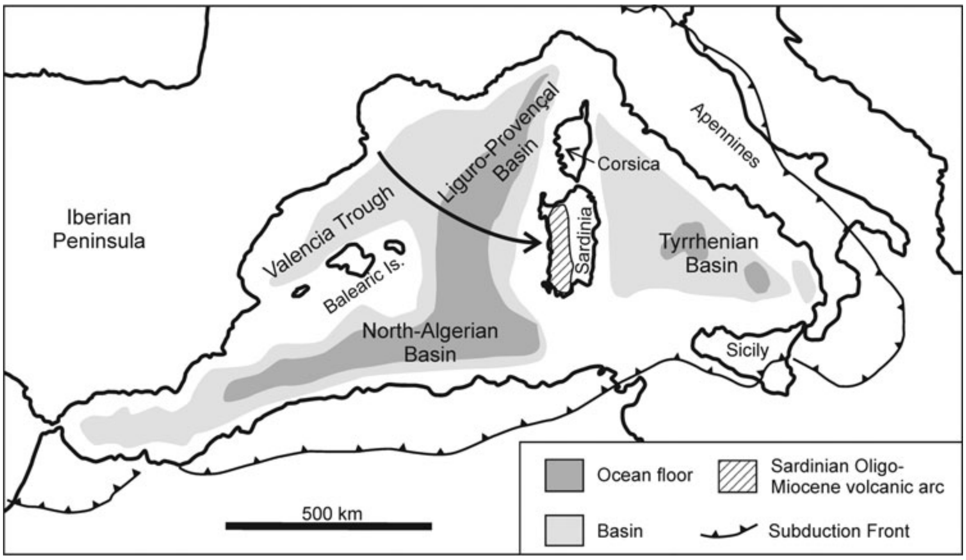

Figure 1. Location of Sardinia in central western Mediterranean. In Oligo-Miocene times Sardinia detached, drifted and rotated from the European continental margin to its current position by roll-back of the Apulian subduction zone (Cherchi & Montadert, 1982; Séranne, 1999; Rollet *et al.* 2002). Abundant subduction magmatism formed in arc position in Sardinia during this time.

magnetism (remanent magnetizations and anisotropies of magnetic susceptibility) (e.g. McIntosh, 1991; Ort, Rosi & Anderson, 1999; Suzuki *et al.* 2005; Ellis *et al.* 2012; Speranza, Di Chiara & Rotolo, 2012; Best *et al.* 2013; Ort *et al.* 2013; Vigliotti, 2015); and whole-rock geochemistry (e.g. Orton, 1992; Gençalioglu-Kuscu & Floyd, 2002; Peate *et al.* 2003; Vidal-Solano *et al.* 2013). Several of these methods can be used in conjunction with each other. In addition, although not strictly used for ignimbrite correlations, Sr, Nd and Pb isotope ratios have also been used in combination with these methods to correlate distal tephras with their parental ignimbrites (e.g. Peate *et al.* 2003).

Whole-rock geochemistry is usually regarded as one of the less appropriate criteria to characterize ignimbrites for their correlation (e.g. Walker, 1972; Hildreth & Mahood, 1985; Orton, 1992). Drawbacks mostly arise from the pyroclastic nature and emplacement mechanisms of these deposits. The final ignimbrite deposit may have a composition different from that of the original magma and it may be chemically heterogeneous due to factors such as: (1) loss of primary pyroclastic components (e.g. fine ash by elutriation) and incorporation of external lithics (e.g. accidental lithics) during the generation, transport and deposition of PDC (Walker, 1972; Wolff, 1985; Branney & Kokelaar, 1992, 2002); (2) heterogeneous deposition of pyroclastic components due to the different characteristics of each particle type (e.g. viscosity, shape or density among others) (Walker, 1972; Branney & Kokelaar, 1992, 2002); or (3) magma supply of changing composition (e.g. due to emission from a zoned magma chamber), which results in the formation of chemically zoned ignimbrites (e.g. Sumner & Branney, 2002; Sumner & Wolff, 2003; Bachmann & Bergantz, 2008).

Despite the wide lack of confidence in whole-rock geochemistry as a correlation tool we propose that, if appropriately used, it can be a valid and highly useful criterion for the correlation of ignimbrite deposits. This is illustrated here by presenting a case of correlation conducted on a Miocene ignimbrite sequence in the Sulcis area of Sardinia (Italy) (Figs 1, 2). In this example, correlation was based on a set of binary diagrams. The approach followed to develop specific diagrams for the Sulcis area is presented here with the purpose of being used as a guide for its implementation in other study areas.

2. Geological background

2.a. Recent geodynamic evolution of Sardinia

The Corsica–Sardinia microplate was part of the European continental margin until the late Oligocene epoch (Séranne, 1999). During the Oligocene epoch, the convergence between African and Eurasian plates triggered the formation of the Apulian subduction zone on the western Mediterranean margin (Rollet *et al.* 2002). Subsequent SE-directed rollback of this subduction zone caused the Corsica–Sardinia microplate to detach, drift and rotate from the European continental margin to its present position during the Oligo-Miocene epochs (Cherchi & Montadert, 1982). As a consequence, the Liguro–Provençal Basin opened between Sardinia and the Iberian Peninsula (Séranne, 1999) and abundant subduction-related calc-alkaline orogenic volcanism occurred in Sardinia in an arc setting, mostly under extensional tectonics (Coulon, 1977) (Fig. 1). The products of this volcanic activity can be found in western Sardinia (Fig. 2).

2.b. Oligo-Miocene magmatism in the Sulcis

In the Sulcis area (SW Sardinia, Fig. 2) the Oligo-Miocene magmatism produced a special volcanic suite. Differently from other areas of the magmatic arc in

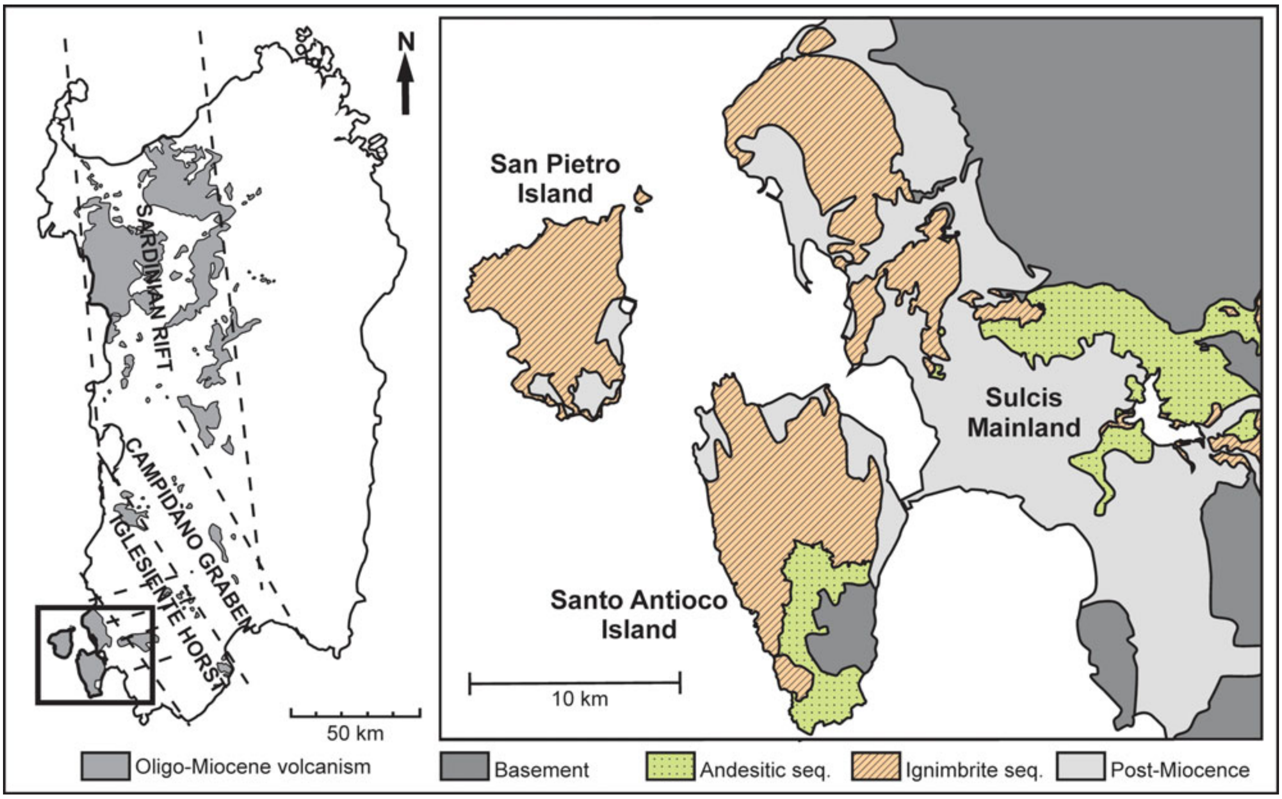

Figure 2. (Colour online) Left: Oligo-Miocene volcanic deposits in Sardinia and main extensional tectonics structures. The square delimits the study area of this work, the Sulcis. Right: the Oligo-Miocene volcanic deposits in the Sulcis area. These consist of a lower andesitic sequence dominated by domes and lava flows and an upper sequence dominated by an ignimbrite stack. Both halves of the sequence are in excess of 400 m thick.

Sardinia, in the Sulcis region magma compositions shifted from subduction-related calc-alkaline at the beginning to mildly alkaline towards the end of the magmatic cycle, including peralkaline rhyolites (Araña, Barberi & Santacroce, 1974; Assorgia *et al.* 1994; Morra, Secchi & Assorgia, 1994; G. Gisbert, unpub. PhD thesis, University of Barcelona, 2012).

The Oligo-Miocene volcanic rocks of the Sulcis were emplaced during 33–15 Ma (Savelli, 1975; Beccaluva *et al.* 1985; Morra, Secchi & Assorgia, 1994; Pasci *et al.* 2001) and are found in mainland Sardinia and in two minor islands (Santo Antioco and San Pietro; Fig. 2). The volcanic sequence consists of: (1) a lower sequence >400 m thick of andesitic (basaltic andesite and andesite) domes and lava flows; and (2) an upper sequence >400 m thick dominantly formed by a stack of ignimbrite sheets (transitional to mildly alkaline with rhyolitic and minor trachytic compositions, and including comendites) (Assorgia *et al.* 1992*b*). The ignimbrite sequence was emplaced during 17–15 Ma (Morra, Secchi & Assorgia, 1994; Pasci *et al.* 2001).

2.c. The ignimbrite sequence of the Sulcis

The stratigraphy of the ignimbrite sequence in the Sulcis was originally established and described from the study of prospective coal mining boreholes performed by the Carbosulcis S.p.A Company in mainland Sulcis (Assorgia *et al.* 1990*a*, *b*, 1992*a*, *b*), and further developed by subsequent studies (Cincotti *et al.* 1992; Morra, Secchi & Assorgia, 1994; Gimeno *et al.* 1996, 2003; L. Pioli, unpub. PhD thesis, Università di Pisa, 2003; Pioli & Rosi, 2005; Pioli *et al.* 2008; Mundula, Cioni & Rizzo, 2009; Mulas, Mundula & Cioni, 2011; G. Gisbert, unpub. PhD thesis, University of Barcelona, 2012; S. Pasci & P. Orrù (coord), unpub. map, Carta Geologica d'Italia, sheet 564 of the 1:50 000 map of the Istituto Geografico Militare, Servizio Geologico d'Italia). The ignimbrite sequence of the Sulcis is currently subdivided into 18 units (term used in this and previous works in the area in a loose sense, without genetic significance) (Table 1, in stratigraphic order). Each of these units consists of one of the following: (1) a simple ignimbrite formed by a single flow unit (CM, LE, SE, NU, MU, CF, SP and PM units); (2) a compound ignimbrite formed by a stack of several flow units as a cooling unit (AC, MC, CA, PC, MZ and PA units); or (3) a complex sequence consisting of a mixture of lava flows and deposits of PDC (MLN, MCR and CO units), erupted during one or several eruptions (e.g. as evidenced by palaeosoils within the CO unit). Except for complex units, most of the described units represent eruptive units formed by individual eruptions. Palaeosoils or reworked materials are typically found separating units, indicating significant time lapses between eruptive events.

Individual ignimbrites in the Sulcis are typically *c.* 10–20 m thick, although thicknesses above 100 m are

Table 1. Main characteristics of the Andesites and ignimbrite units. Units in stratigraphic order. Mineral abbreviations: amp – amphibole; ano – anorthoclase; bt – biotite; cpx – clinopyroxene; ol – olivine; opq – opaque mineral; opx – orthopyroxene; pl – plagioclase; px – pyroxene; qz – quartz; sa – sanidine; zrn – zircon; a.m. – altered mafic; (v) – vapour phase. Mineral assemblage was studied and described by G. Gisbert (unpub. PhD thesis, University of Barcelona, 2012).

Unit	Phenocryst content (vol %)	Mineral assemblage	Main characteristics
CL/PG	10	Sa + pl + opq ± zrn	Colonne/Punta Genniò: Mundula, Cioni & Rizzo (2009). Moderately welded cineritic ignimbrite.
PM	<1	sa + ano + pl + opq + m.a. ±zrn	Punta Mingosa: Mundula, Cioni & Rizzo (2009). Moderately welded aphyric cineritic single flow unit ignimbrite.
SP	1–20	pl + ano + opq + px + amp	Serra di Paringianu: Assorgia *et al.* (1990*a*). Extremely welded and eutaxitic single flow unit ignimbrite. Abundant extremely flattened light and dark grey pumices. Basal vitrophyre. Non-welded facies in northern San Pietro and Santo Antioco islands.
PA	<10	sa + pl + opq ± bt ± zrn	Paringianu: Assorgia *et al.* (1990*b*). Scarcely to moderately welded compound ignimbrite. Mostly cineritic. Low porphyricity and pumice content.
CF	10–20	sa + opq + ano	Carloforte: G. Gisbert, unpub. PhD thesis, University of Barcelona, 2012. Peralkaline. Strongly welded and eutaxitic single flow unit ignimbrite with abundant sanidine-bearing black pumices. Also grey and white pumices.
MU	<3	sa + qz + opq + amp(v)(±zrn)	Monte Ulmus: Assorgia *et al.* (1990*a*). Peralkaline. Stronlgy welded and eutaxitic aphyric single flow unit ignimbrite with occasional scarce black strongly flattened pumices. Basal vitrophyre.
CO	5–30 up to 50	sa + qz + amp + opq + amp(v)	Comendites: Assorgia *et al.* (1990*b*). Peralkaline. Complex unit. Lava flows and variably welded ignimbrites with or without basal vitrophyre. May contain quartz phenocrysts.
MZ	3–20	pl + bt + opq	Matzaccara: Assorgia *et al.* (1990*a*). Variably welded complex ignimbrite unit formed by several flow units. Presents abundant bronze-coloured biotite.
MCR	5–20	sa + pl + opq ± zrn	Montagna di Capo Rosso: Mundula, Cioni & Rizzo (2009). Lava flows and moderately welded lithic rich ignimbrites.
PC	up to 50	ano + pl + opq + cpx + opx	Punta dei Cannoni: Mundula, Cioni & Rizzo (2009). Moderately to strongly welded, eutaxitic and porphyritic compound ignimbrite. Abundant big (several dm) pumices.
NU	20–30	sa + pl + opq + cpx ± amp(v)	Nuraxi: Assorgia *et al.* (1990*b*). Extremely welded and eutaxitic single flow unit ignimbrite. Scarce extremely flattened grey pumices. Rheomorphic structures are abundant. Basal vitrophyre.
CA	10	sa + pl + opq	Conca is Angius: Assorgia *et al.* (1990*b*). Slightly welded compound ignimbrite. Abundant pumices and accidental lithics. Degassing structures present.
MC	10–20	sa + pl + opq + amp(v)	Monte Crobu: Assorgia *et al.* (1992*a*). Moderately to extremely welded and eutaxitic compound ignimbrite formed by two flow units. Abundant to dominant grey and occasionally black strongly flattened pumices. Rheomorphic. Basal vitrophyre.
MLN	<5	pl + opq ± bt	Monte la Noce: Pasci and Orrù (unpub. map, 2016). Lava flows, cinerites and moderately to extremely welded ignimbrites with basal vitrophyre. Mostly nearly aphyric.
SE	10–20	pl + opq + m.a. ± opx ± cpx + amp(v)	Seruci: Assorgia *et al.* (1990*b*). Highly welded and eutaxitic single flow unit ignimbrite with dm-sized pumices. Basal vitrophyre.
AC	10–20	pl + bt + opq ± amp	Acqua sa Canna: Assorgia *et al.* (1990*b*). Poorly welded compound ignimbrite formed by several flow units with pumice normal grading. Locally lithic-rich.
LE	10–20	pl + sa + opq + opx ± zrn	Lenzu: Assorgia *et al.* (1990*b*). Strongly welded and eutaxitic single flow unit ignimbrite. Abundant dm-sized pumices. Basal vitrophyre.
CM	10–30	pl + cpx + opq ± bt ± amp	Corona Maria: Assorgia *et al.* (1990*b*). Scarcely to moderately welded and eutaxitic single flow unit ignimbrite. Abundant pumices and lithic fragments. Basal vitrophyre.
AND		pl + opx + cpx + opq ± ol	Andesites: Assorgia *et al.* (1990*b*). Lava flows and domes with associated breccias.

reported in some sites (Assorgia *et al.* 1992*b*). Areas covered by each one are on the order of a few hundred square kilometres (Assorgia *et al.* 1992*b*). Most flow units share a common structure described by Assorgia *et al.* (1990*a*, *b*) (Fig. 3): (1) fine-grained loose basal layer some centimetres to decimetres thick, whitish in colour, rich in free crystals and pumices; (2) vitrophyre layer of variable thickness (typically from a few decimetres to half a metre), black in colour and poorly porphyritic at the bottom, transitional to the central body at the top; (3) central body, in most units consisting of eutaxitic facies and showing variable degrees of welding and a massive to fluidal fabric; and (4) upper part, which is a less welded portion, rich in pumices within an ash matrix. The main, and sometimes only, component of all flow units is the central body, which constitutes most of their thickness. The other three layers may or may not have been formed or preserved.

A brief summary of the characteristics of each ignimbrite unit is given in Table 1. A detailed description of the ignimbrite units can be found in previous works (Assorgia *et al.* 1990*a*, *b*, 1992a, *b*; Cincotti *et al.* 1992; Morra, Secchi & Assorgia, 1994; Gimeno *et al.* 1996, 2003; L. Pioli, unpub. PhD thesis, Università di

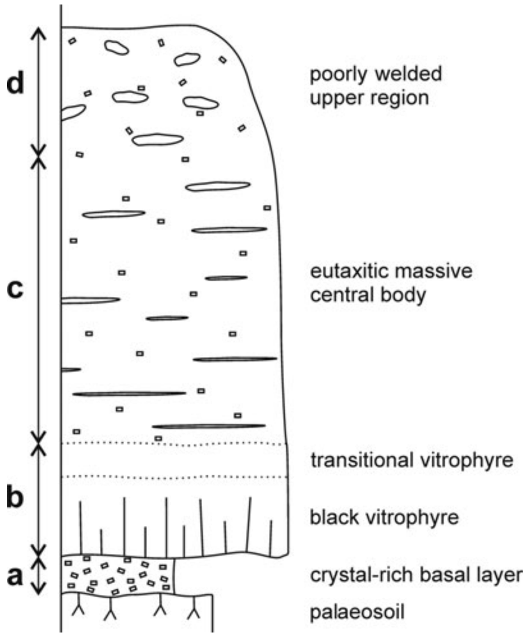

Figure 3. Schematic diagram of the dominant structure of ignimbrite flow units in the Sulcis as described by Assorgia *et al.* (1990*a*, *b*). Thicknesses are not to scale and may vary significantly between different ignimbrites.

Pisa, 2003; Pioli & Rosi, 2005; Pioli *et al.* 2008; Mundula, Cioni & Rizzo, 2009; Mulas, Mundula & Cioni, 2011; G. Gisbert, unpub. PhD thesis, University of Barcelona, 2012; S. Pasci & P. Orrù (coord), unpub. map, Carta Geologica d'Italia, sheet 564 of the 1:50 000 map of the Istituto Geografico Militare, Servizio Geologico d'Italia), as well as in a summary of these descriptions in the online Supplementary Material 1 (available at http://journals.cambridge.org/geo).

The lower half of the ignimbrite sequence (CM to CA units) was formed by trachydacitic (CM, AC) and rhyolitic (LE, SE, MLN, MC, CA) magmas with compositions transitional between calc-alkaline and mildly alkaline (G. Gisbert, unpub. PhD thesis, University of Barcelona, 2012). These magmas were emplaced as both weakly and strongly to extremely welded ignimbrites. In this lower part of the sequence, units containing strongly welded flow units tend to alternate with others consisting of scarcely welded flow units. Flow units in Corona Maria (CM), Acqua sa Canna (AC) and Conca is Angius (CA) units are scarcely welded, whereas those in Lenzu (LE), Seruci (SE) and Monte Crobu (MC) units are strongly welded. CM, LE and SE units consist of one single flow unit each. AC, MC and CA units are compound ignimbrites formed by several flow units. Monte la Noce (MLN) unit combines lava flows and pyroclastic density current deposits with various degrees of welding. CM, LE, AC, SE and CA units crop out mostly in the northern mainland of the study area (map in Supplementary Material 1). The MLN unit crops out exclusively in a limited area of eastern Santo Antioco Island. The MC unit crops out in the southern mainland and on Santo Antioco Island.

After the emplacement of the CA unit, magma compositions shifted to mildly alkaline, both trachydacitic (PC, MZ) and rhyolitic (NU, MCR) (G. Gisbert, unpub. PhD thesis, University of Barcelona, 2012). Whereas Punta dei Cannoni (PC) and Montagna di Capo Rosso (MCR) units are restricted to western San Pietro Island, Nuraxi (NU) and Matzaccara (MZ) are the two most widespread units in the ignimbrite sequence. These two units cover the whole study area. The NU unit covers at least 600 km^2 (Pioli & Rosi, 2005), which with an average thickness of about 20 m represents a minimum volume of 12 km^3. This unit has been one of the most studied in the area (e.g. Gimeno *et al.* 1996, 2003; L. Pioli, unpub. PhD thesis, Università di Pisa, 2003; Pioli & Rosi, 2005; Pioli *et al.* 2008). It contains abundant rheomorphic structures and, in pumice-poor facies, it is lava-like due to its extreme welding and rheomorphism. The NU unit consists of a single flow unit. On the contrary, the MZ unit is formed of several flow units with a large variation in lithofacies, without evidence of a significant time lapse between their emplacements. Except on San Pietro Island, where it can be found in strongly welded facies, the MZ unit presents a weakly welded character and is thin (few metres). Despite its facies variability, the MZ unit is characterized by the presence of abundant bronze-coloured biotite, which is a mineral either rarely found or absent in the rest of the units.

After MZ unit emplacement, magma compositions shifted to perakaline and three units of comenditic composition were formed: Comendites (CO); Monte Ulmus (MU); and Carloforte (CF) (G. Gisbert, unpub. PhD thesis, University of Barcelona, 2012). The CO unit is a complex unit consisting of several weakly to strongly welded ignimbrites and lava flows (the latter only in northern San Pietro Island; their study at the locality of Le Commende in this island resulted in the definition of the comenditic rock type by Bertolio, 1895). Palaeosoils within the ignimbrites and lava flows sequence indicate a protracted time span for the emplacement of the whole unit. The MU unit consists of a single strongly welded flow unit which has its maximum expression in western Santo Antioco Island. The Carloforte unit was defined by G. Gisbert (unpub. PhD thesis, University of Barcelona, 2012); it had been previously considered to be part of Monte Ulmus unit (Mulas, Mundula & Cioni, 2011). This unit consists of a single strongly to extremely welded flow unit and is characterized by containing abundant large highly porphyritic black pumices. It has its maximum development in San Pietro Island. The CO and MU units crop out in both minor islands and in the central mainland. The CF unit crops out in the central mainland and in San Pietro Island.

After the emplacement of the peralkaline units, erupted magmas returned to mildly alkaline and transitional compositions (G. Gisbert, unpub. PhD thesis, University of Barcelona, 2012). The upper section of the ignimbrite sequence consists of two widespread units (PA and SP) and two minor geographically restricted units

(PM and CL/PG) of rhyolitic composition. The Paringianu (PA) unit is a compound ignimbrite formed by several mostly non-welded flow units. Serra di Paringianu (SP) is the latest widespread ignimbrite. It covers the whole study area and is a simple ignimbrite formed by a single flow unit. SP unit is characterized by a thick basal vitrophyre and its extreme welding (except for a particular facies in northern San Pietro and Santo Antioco islands). Pumice-poor facies of the SP unit may be very similar to the NU unit. Both PA and SP are found in the mainland and in both minor islands. The Punta Mingosa (PM) unit consists of a simple ignimbrite formed by a single welded flow unit, and its distribution is restricted to southern San Pietro Island.

The mineral assemblage of ignimbrites in the Sulcis (see Table 1) is dominated by feldspars (plagioclase ± anorthoclase ± sanidine), accompanied by opaque minerals (Fe and Ti oxides) and accessory mafic minerals. These mafic minerals are mainly pyroxenes, with presence in some units of amphibole or biotite. Quartz is an essential mineral phase in comenditic deposits except in obsidianaceous facies, whereas it is not found in deposits of other compositions. Zircon and apatite occur as accessory minerals in some units. Vapour phase amphibole crystals, which may appear as poikilitic laths in the matrix (in comendites) or as hypidiomorphic crystals in vesicles (miarolitic texture in peralkaline or nearly peralkaline units), may be present.

Only a few of the units defined in the Sulcis present characteristic features such as the presence of a specific mineral phase (e.g. bronze-coloured biotite in MZ) or pumice type (e.g. porphyritic black pumices in CF unit). Instead, strong lithologic similarities usually exist between different units (macroscopically and even microscopically), especially between the porphyritic welded units (e.g. between some NU and SP facies; Fig. 4). In addition, some units present a wide facies variability (occasionally individual facies resembling those of other units). As a consequence, correlation is strongly hampered when outcrop continuity is scarce and/or the stratigraphic position cannot be established. This situation motivated the search for a complementary identification and correlation tool to be used in this area for the successful study of the ignimbrite sequence.

3. Analytical procedures

A total of 242 samples were prepared for whole-rock geochemical analysis. These included both representative samples of each of the studied ignimbrite units to characterize their geochemistry, and samples collected from problematic outcrops or facies to be identified.

A representative amount of each sample was ground to powder in a tungsten carbide rings mill after removing external lithic fragments (e.g. accidental clasts, clasts collected by the PDC during transport) and weathered parts. Results indicate that the mill contributed variable amounts of Ta and W, whereas no significant contribution of Nb was observed. Rock samples collected at or near (less than 200 m) the coast were treated to remove marine salts (rock slice bath in distilled water); no significant differences were observed in obtained chemical compositions between treated samples and samples that did not require treatment from equivalent origin (same lithofacies, same unit). Samples were prepared at the facilities of the Faculty of Geology of the University of Barcelona. The same rock powder was used for all analyses of major and trace elements.

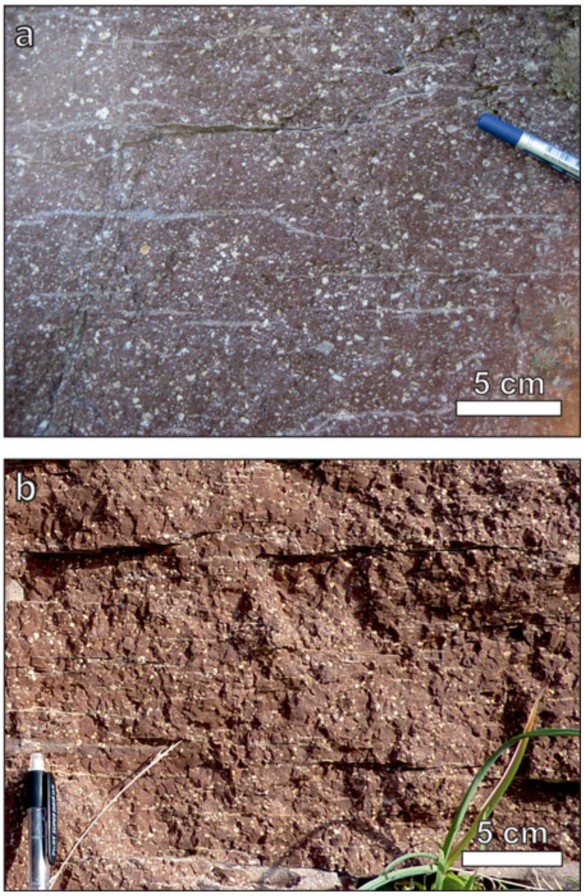

Figure 4. (Colour online) Example of strong similarity between two different ignimbrites in the Sulcis. Extremely welded and eutaxitic facies of (a) Nuraxi and (b) Serra di Paringianu units.

All 242 samples were analysed for major and trace elements using X-Ray Fluorescence (XRF) and low blank fused pearls and pressed pellets at the Centres Científics i Tecnològics of the Universitat de Barcelona (CCITUB) on a Philips PW2400 sequential X-Ray spectrometer. The instrument was calibrated using 64 rock standards. International reference standard JB-3 (Imai *et al.* 1995) was repeatedly measured as unknown to monitor precision and accuracy. For major elements, analytical precision (1σ, $n = 12$) was better than 1 % for SiO_2, Al_2O_3 and CaO, 2 % for TiO_2, Fe_2O_3, MgO and K_2O, 3 % for MnO and P_2O_5, and 6 % for Na_2O. For trace elements, precision (1σ, $n = 20$) was better than 5 % for Ba, Sr and Zr, 8 % for Y, 14 % for Nb, 21 % for Pb, 27 % for Rb and 42 % for Th. The apparent low precisions for Nb, Pb, Rb and Th are due to the low contents of these elements in JB-3 (2.5 ppm Nb, 5.6 ppm Pb, 15 ppm Rb, 1.3 ppm Th), which fall at the lower end or below the calibration range. These errors are therefore maximum estimates. The studied samples have significantly higher contents for these elements (26–107 ppm Nb, 17–48 ppm Pb, 125–286 ppm Rb, 10–27 ppm Th), and they therefore likely have significantly better precisions, similar to those of Ba and Zr.

A subset of 92 of the most fresh and representative samples was analysed with inductively coupled plasma with optical emission spectrometry (ICP-OES) and inductively coupled plasma with mass spectrometry (ICP-MS) at the CCITUB for more precise trace elements. These analyses were performed on an ICP-OES Perkin Elmer Optima 3200 RL and an ICP-MS Perkin Elmer Elan 6000. Analytical precision (JB-3, 1σ, $n = 5$) was better than 4 % for Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, and 7.4 % for U.

Continuous trends in variation diagrams show that there was no significant nugget effect affecting susceptible elements such as Ti, Zr or rare earth elements (REE) due to either non-representative sampling or incomplete acid dissolution for ICP analyses.

Loss on ignition (LOI) was performed for all samples undergoing geochemical analyses at the CCITUB.

The procedures for sample preparation for XRF and ICP analyses and LOI determination are described in the online Supplementary Material 2 (available at http://journals.cambridge.org/geo).

4. Methodology

Several factors influenced which of the complementary correlation and identification criteria listed in the Introduction (Section 1) could be used in the Sulcis ignimbrite sequence: (1) large number of ignimbrite units (18); (2) strong welding in many of them; (3) rare preservation of the juvenile pyroclasts (glass devitrification; G. Gisbert, unpub. PhD thesis, University of Barcelona, 2012); and (4) sequence emplacement in a small time span (about 3 Ma; Araña, Barberi & Santacroce, 1974; Montigny, Edel & Thuizat, 1981; Boni, Del Vecchio & Lirer, 1990; Garbarino *et al.* 1990; Maccioni, Marchi & Assorgia, 1990; Morra, Secchi & Assorgia, 1994; Pasci *et al.* 2001). Under these conditions, whole-rock geochemistry represented the most viable complementary method for unit correlation, as will be argued in the Discussion (Section 6). A graphical approach based on binary diagrams was chosen based on the criteria of ease of use and sharing with other researchers working in the area.

4.a. Building of the geochemical database

The first step in the development of the correlation tool was to build a comprehensive geochemical database containing all the available published and new geochemical data for the study area. Literature data were collected from: Araña, Barberi & Santacroce (1974), Assorgia *et al.* (1994), Morra, Secchi & Assorgia (1994), Cioni & Funedda (2005), and Conte *et al.* (2010), as well as from two unpublished studies (L. Ramon Sala, unpub. minor thesis, Universitat de Barcelona, 2009; Z. Roselló Espuny, unpub. minor thesis, Universitat de Barcelona, 2005).

Only geochemical data with good analysis quality and accurate attribution to their ignimbrite unit were incorporated into the database. Analyses with major elements totals under 98 wt % or LOI above 2.5 wt % (limit value for a rock to be considered fresh fixed in Le Maitre *et al.* 1989) were rejected. Vitrophyres were an exception to the specified LOI requirement because their glass may contain up to 7 wt % volatiles in fresh condition (Smith, Tremallo & Lofgren, 2001); volatiles in fresh vitrophyres occur dissolved in glass, not in secondary minerals. Each analysis was compared with the rest of data from the same ignimbrite unit to check for data consistency; clear outliers were rejected. The complete database is provided in online Supplementary Material 3 (available at http://journals.cambridge.org/geo).

Next, the most suitable elements to be used in the binary diagrams were explored.

4.b. Selection of chemical elements for the diagrams

Major elements (except for Ti) were considered of little use for discrimination between units in the Sulcis because of: (1) similarity in compositions between many of the ignimbrite units (e.g. Fig. 5; also seen in Harker diagrams (not shown)); and (2) high mobility of most of these elements during alteration and weathering processes (Winchester & Floyd, 1977), which preferentially affect non-welded deposits. The selection of elements for binary diagrams was therefore mostly centred on trace elements.

Among trace elements, selection was focused on immobile trace elements to minimize the possible effects of alteration and weathering. Many immobile trace elements have been repeatedly used in the literature to characterize the chemistry and affinity of volcanic deposits and suites, mostly of ancient deposits (e.g. Zr, Y, Nb and Nd; Winchester & Floyd, 1977; Leat *et al.* 1986).

Binary diagrams may represent individual elements and/or element ratios. To maximize separation of different ignimbrites or units, it is convenient to combine trace elements or element ratios which are controlled by different processes (e.g. differentiation degree, alkalinity). For example, ratios between trace elements such as Zr, Y and Nb, in combination with Ti, are known to monitor chemical variability related to magmatic differentiation degree (e.g. Zr/TiO_2; Winchester & Floyd, 1977) or alkalinity (e.g. Nb/Y; Pearce & Cann 1973; Floyd & Winchester, 1975; Winchester & Floyd, 1977).

Ratios used as a proxy for the magma differentiation degree consist of a ratio between a compatible and an incompatible element. Progressive depletion of the compatible element and enrichment of the incompatible element during magma differentiation by fractional crystallization produce a steady modification of

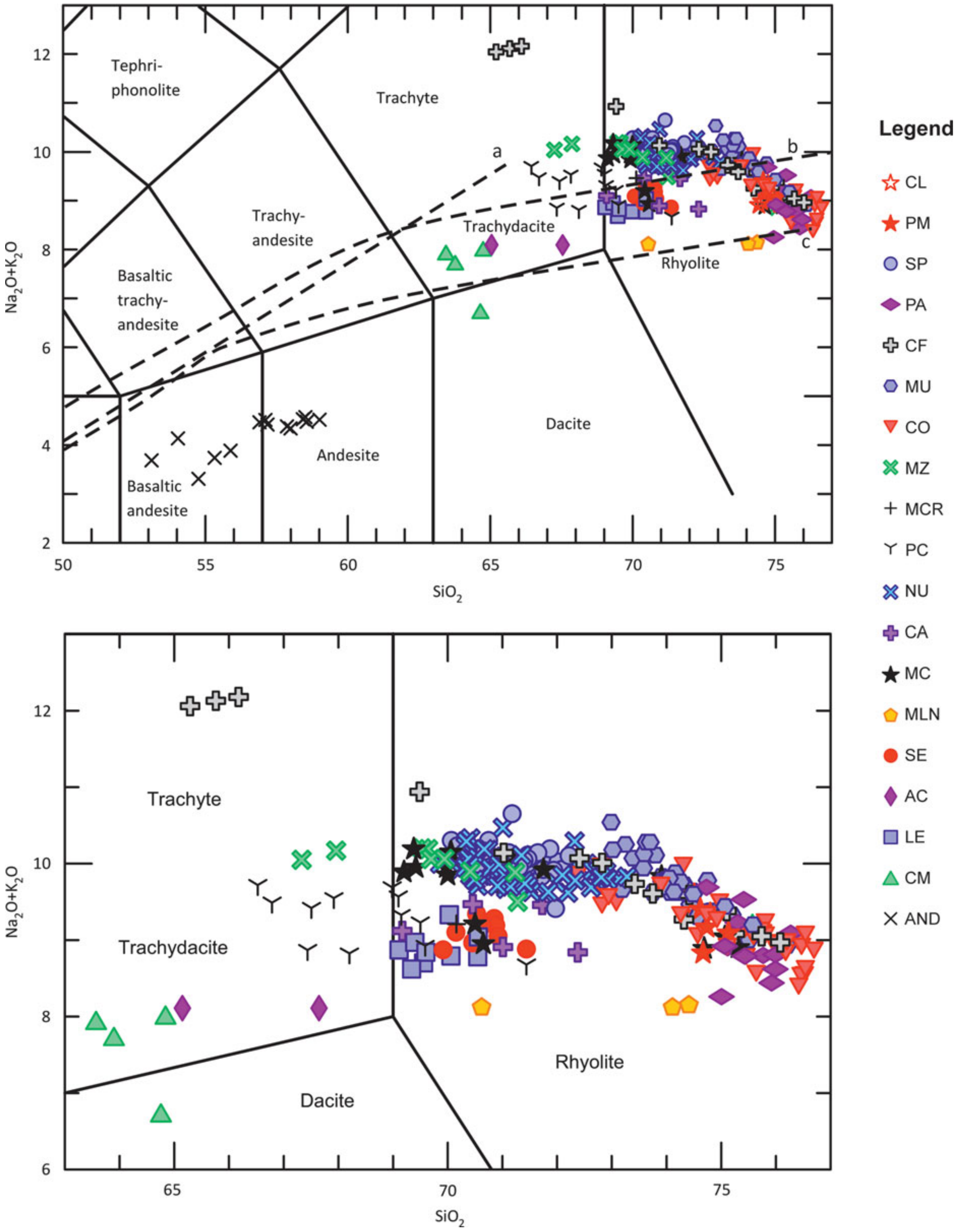

Figure 5. (Colour online) Upper diagram: Partial view of the Total Alkalis versus Silica diagram (Le Bas *et al.* 1986) showing the compositions of the ignimbrite units and andesitic sequence in the Sulcis area. Lower diagram: detail of the ignimbrite sequence compositions. Strong major-element chemical similarity of the most-evolved units produces their overlapping. Contents in wt %. Dash lines are the subdivision of volcanic rocks into alkaline (above) and subalkaline (below) as proposed by: (a) MacDonald (1968); (b) Irvine & Baragar (1971); and (c) Kuno (1966).

the ratio between both elements. A widely used ratio is Zr/TiO_2 (e.g. Winchester & Floyd, 1977; Fig. 6a for the Sulcis). This ratio increases with differentiation due to the contrasting behaviour of TiO_2 and Zr (compatible and incompatible, respectively). Two main factors must be considered when using an incompatible/compatible element ratio in pyroclastic deposits: (1) consistent behaviour of the chosen elements throughout the whole compositional range of the studied materials; and (2) the possible effects of differential deposition of

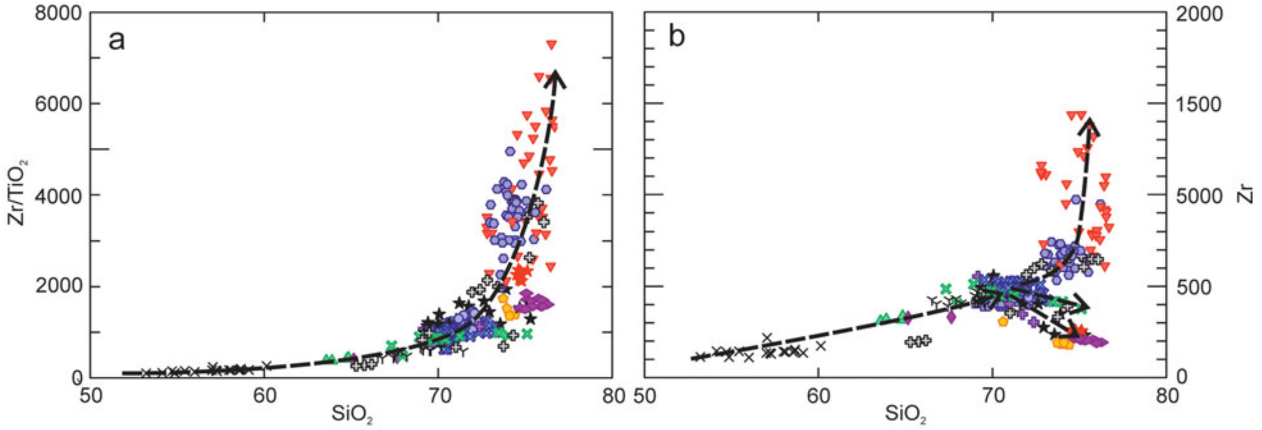

Figure 6. (Colour online) (a) Positive correlation between Zr/TiO_2 and SiO_2 in the Sulcis volcanics showing that this ratio can be used as a proxy for differentiation degree; and (b) behaviour of Zr with differentiation in the Sulcis magmas. Beyond 70 wt % SiO_2 significant zircon precipitation produces a decline in Zr concentration in the less alkaline magmas, whereas peralkaline magmas are constantly enriched. SiO_2 and TiO_2 concentrations in wt %, Zr concentration in $\mu g\ g^{-1}$. Symbols as for Figure 5.

pyroclastic components in the studied flow unit. These factors are addressed next.

For the incompatible/compatible element ratio to remain a useful indicator of magma differentiation, both chosen elements should consistently behave as incompatible and compatible during the whole studied compositional range. Continuing with the example of the Zr/TiO_2 ratio, whereas TiO_2 is consistently compatible in the most common fractionating mineral assemblages, Zr may shift from incompatible to compatible if zircon fractionation occurs. In the Sulcis magmatism (Fig. 6a), fractional crystallization of a mineral assemblage without either quartz or zircon produced a positive correlation between SiO_2 and Zr/TiO_2 from andesitic compositions to SiO_2 contents around 73 wt %. An increase in the Zr/TiO_2 ratio results from TiO_2 depletion mostly due to fractionation of Fe-Ti oxides. Above 73 wt % SiO_2, two different behaviours can be observed in Sulcis magmas. In the most evolved magmas of less alkaline compositions (MLN, CA, MC, PA and PM units), zircon joins the fractionating mineral assemblage above *c.* 70 % SiO_2 (Fig. 6b). In this particular case, however, strong TiO_2 depletion compensates the minor zircon fractionation. This results in a still increasing Zr/TiO_2 ratio, which therefore remains useful as a differentiation degree indicator. On the other hand, in the more alkaline magmas zircon saturation is not reached. The most evolved magmas among the more alkaline compositions, those which formed the peralkaline units (CO, MU and CF units), show vertical trends in the SiO_2 v. Zr/TiO_2 diagram that result from quartz saturation and fractionation. Quartz fractionation precludes any further increase of the SiO_2 content in these magmas with continuing differentiation, whereas Zr/TiO_2 continues increasing. For these highly evolved magmas, the Zr/TiO_2 ratio is therefore a better indicator of differentiation degree than SiO_2.

From the example provided with the magmas from the Sulcis, it is demonstrated that the Zr/TiO_2 ratio is especially useful in alkaline and peralkaline magmatic suites due to increased Zr solubility that prevents significant zircon fractionation (Watson, 1979; Watson & Harrison, 1983; Conte & Dolfi, 2002). In study areas with subalkaline magmatic suites, the usefulness of the Zr/TiO_2 ratio may be reduced towards the evolved compositions due to high zircon fractionation. A similar assessment to that presented here for the Zr/TiO_2 ratio in the Sulcis should be conducted for any incompatible/compatible element ratio which could be used.

The second factor to consider when dealing with incompatible/compatible element ratios is related to the deposition mechanisms of PDC. Compatible elements are preferentially concentrated in the mineral fraction of the pyroclastic material, whereas incompatible elements are mostly located in the glass fraction. Differential deposition of mineral and glassy fractions upon emplacement of the ignimbrite may therefore produce heterogeneity of the studied elemental ratio along the ignimbrite deposit. Phenocryst-rich portions of the deposit will be enriched in compatible elements and depleted in incompatible elements (lower incompatible/compatible element ratios), and the opposite will be true for phenocryst-poor areas. Upon sampling the ignimbrite deposit, this effect will produce a wider compositional range of the studied ratio than that of the original magma. In the Sulcis, consistent continuous trends in binary diagrams and relatively limited compositional ranges of incompatible/compatible elements ratios indicate a minor effect of this factor for most units. The preferential enrichment/depletion of compatible/incompatible elements along a given ignimbrite deposit must be also considered if working with a single element instead of an element ratio.

Ratios between incompatible elements are less affected by magma differentiation degree (compared to element ratios containing compatible elements), as well as by differential phenocrysts enrichment/depletion during ignimbrite deposition. Variations in these elements are therefore mostly controlled by other parameters such as initial magma source compositions or melting degree, both controlling initial magma composition (e.g. Nb/Y as a proxy for alkalinity, Pearce &

Cann 1973; Floyd & Winchester, 1975; Winchester & Floyd, 1977). In subduction settings it may be appropriate to investigate incompatible fluid mobile elements (e.g. Rb, as long as there is no significant K-feldspar or biotite fractionation), as these may separate magmas according to the contribution of subduction fluids to their composition. However, the use of these mobile elements can be problematic in case of significant alteration or weathering of the studied materials.

Ratios such as Zr/TiO_2 and Nb/Y have been traditionally used for separating magmas according to their differentiation degree (e.g. Winchester & Floyd, 1977) or alkalinity (e.g. Pearce & Cann 1973; Floyd & Winchester, 1975; Winchester & Floyd, 1977) and, when combined in a single diagram, they provide a powerful tool for discriminating magmas series and rock types (e.g. Winchester & Floyd, 1977). In this work, we use them to discriminate between volcanic units in a single magmatic suite. Small differences in the initial composition of parental magmas (e.g. slight variations in alkalinity or subduction fluids contribution), combined with various degrees of differentiation, may produce significant geochemical differences between magmas forming each ignimbrite. These may be enough to allow their chemical characterization and separation, as is shown here for the Sulcis ignimbrite sequence.

In each particular magmatic suite, the most useful elements and ratios for unit discrimination in binary diagrams may vary, and these need to be empirically explored. In the Sulcis, the Nb v. Zr/TiO_2 diagram was found to be the most useful one (Nb alone produced better unit separation than Nb/Y). Other complementary diagrams were built by searching minor chemical differences between chemically similar units. Although immobile trace elements were initially prioritized, other more mobile elements such as Rb, Sr and Zn were also used because they proved to be highly useful in the Sulcis.

5. Results

Two sets of binary diagrams were produced which allow identification of most ignimbrite units in the Sulcis when stratigraphic position cannot be determined (e.g. small isolated outcrops, enclaves of ignimbrite material within other ignimbrites, isolated samples from boreholes) and macroscopic lithologic characteristics and petrographic observation are not enough. One set is designed to differentiate between similar lithofacies of two different units when attribution doubts exist, for example extremely welded facies of NU and SP units (Fig. 4) which can be separated using a Rb v. Zr/TiO_2 diagram (Fig. 7). This first set of diagrams is provided as online Supplementary Material 4 (available at http://journals.cambridge.org/geo). The other set is aimed at the identification of the ignimbrite unit to which a sample belongs without any previous approximate attribution. In this case, the chemistry of a given sample is projected into successive binary diagrams.

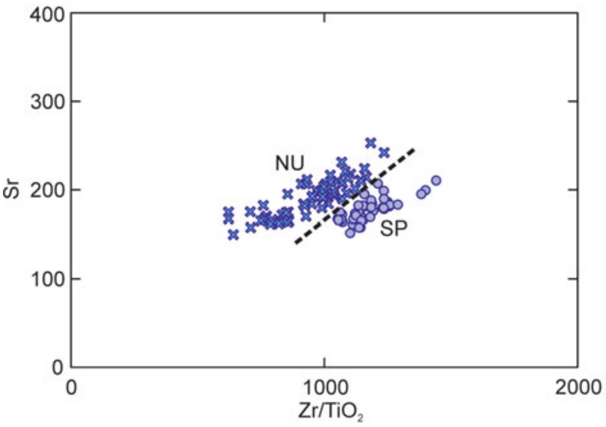

Figure 7. (Colour online) Rb v. Zr/TiO_2 diagram to solve doubts in recognition between NU and SP units. Sr and Zr contents in $\mu g\ g^{-1}$, TiO_2 content in wt%. Symbols follow Figure 5.

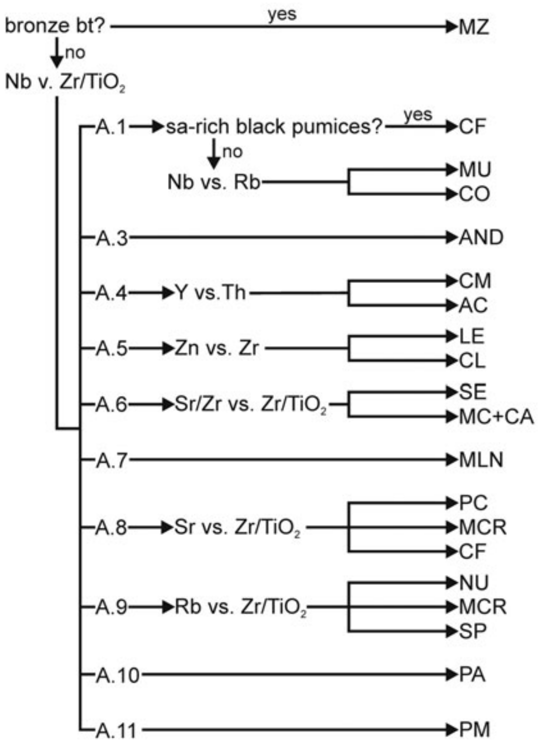

Figure 8. Flow diagram showing the procedure for unit recognition in the Sulcis. The required diagrams are provided in Figure 9.

These progressively separate the different ignimbrite units into various fields following the procedure depicted in Figure 8 until the ignimbrite unit is finally identified.

The identification process of an unknown sample starts with the Nb v. Zr/TiO_2 diagram (Fig. 9, INITIAL), which separates the ignimbrite units into two main areas: Area 1 (A.1) contains the peralkaline units; and A.2 includes the rest of the units. A.2 is subdivided into smaller areas (Fig. 9, A.2), some of which include a single unit (in grey). If a sample falls within one of these single unit areas, it can be readily identified. If a sample plots in an area containing several units (in white), the

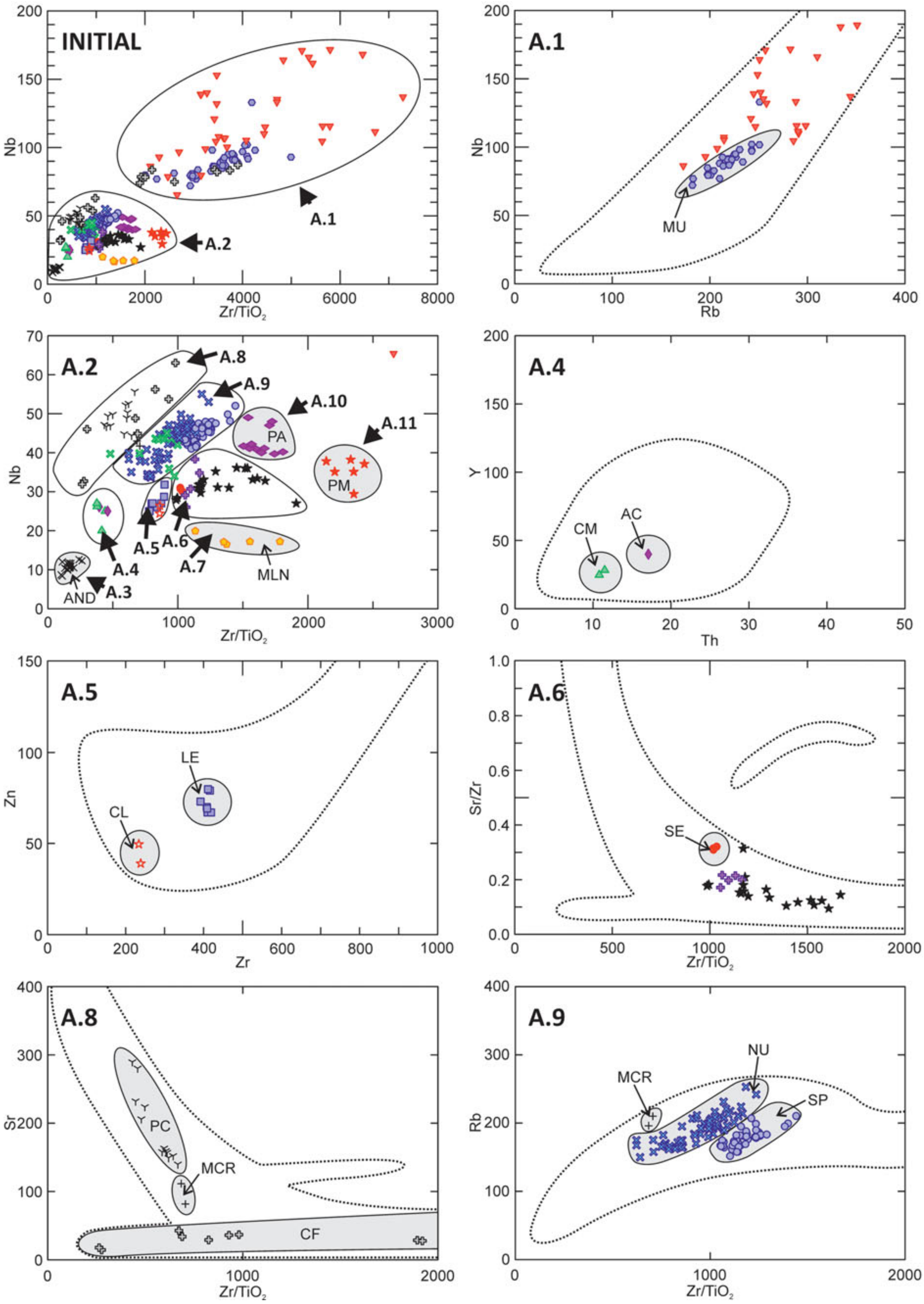

Figure 9. (Colour online) Set of diagrams to be used in the Sulcis to recognize an ignimbrite sample using whole-rock geochemical composition following indications in Figure 8. INITIAL is the first diagram to be used. Diagram names (e.g. A.2, A.3) indicate that a given diagram is to be used to identify samples which fall in the area of that same name in a previous diagram (e.g. diagram A.4 is used to separate units falling in the Area 4 (A.4) of diagram A.2). Areas in grey contain a single unit, allowing immediate identification of the ignimbrite unit. For samples falling within shared areas (white) the use of subsequent diagrams is required, following indications in Figure 8. TiO_2 concentration in wt %, trace element concentrations in $\mu g\ g^{-1}$. Symbols as for Figure 5. The dotted lines contain the areas covered by the chemical variability of the whole Sulcis suite.

subsequent use of a complementary diagram is needed, following indications in Figure 8. Figure 9 provides the different diagrams which may be used for unit identification; in this figure diagrams have the name of the area they solve. These diagrams can be easily used by any researcher working in the Sulcis area to solve doubts in unit identification and correlation.

5.a. Limitations

Although most ignimbrite units in the Sulcis can be identified using only whole-rock geochemistry, in a few of the 18 ignimbrite units it was not possible to completely separate and characterize them. This was due to either lack of enough quality data (e.g. CM and AC units), wide compositional range (e.g. MZ) or compositional similarity between two or more units (e.g. MC and CA, MU and CF).

In the case of the MZ and CF units, they are lithologically and petrographically distinctive, which makes the use of geochemistry unnecessary for their recognition. The MZ unit is characterized by the abundance of bronze-coloured biotite phenocrysts, which are rare to absent in the rest of the ignimbrite units. The CF ignimbrite is characterized by abundant porphyritic black pumices, which are rich in sanidine cumulate phenocrysts (G. Gisbert, unpub. PhD thesis, University of Barcelona, 2012). Chemical compositions of the CF unit deposits are controlled by black pumice abundance and depict a mixing line between a pumice-rich trachytic end-member and a pumice-poor comenditic one (Fig. 5).

The CM and AC units are rich in lithic fragments. Available chemical data are mostly from literature (samples from boreholes) and present a wide compositional scatter that is attributed to deficient removal of the lithic fragments during preparation. This scattering prevents an effective separation of these two units in binary diagrams. New data obtained in this study (where careful removal of lithic fragments was conducted) are scarce but seem to indicate that a Y v. Th diagram may be adequate for the chemical differentiation of these two units (Fig. 9, A.4).

The MC and CA units show very similar compositions, which precludes their chemical separation. These two units present a separated geographical distribution (MC in the south of the study area, CA in the north) with just a minor overlap in northern Santo Antioco island. While in the separate areas these units present strongly different lithofacies which prevent any misidentification (e.g. MC is usually highly welded, whereas CA is not welded), in the overlapping area the contact between both units is not exposed and a lithofacies transition between both units seems to be present. It is suggested that chemical similarity may be due to both units being the deposits of a single eruptive event. MC and CA would then represent two different lithofacies of the same eruptive unit. Further investigation of the stratigraphy of this part of the ignimbrite sequence is needed.

6. Discussion

6.a. Whole-rock geochemistry versus other complementary correlation criteria

Several criteria are commonly used in the correlation of ignimbrite deposits as complements to stratigraphic correlation in the field and lithological and petrographic observation (see Section 1, Introduction). Whole-rock geochemistry presents some advantages with respect to other correlation techniques that were determining for the selection of this technique for ignimbrite correlation in the Sulcis suite.

(1) *Large number of variables*. This is the main advantage of whole-rock geochemistry, which is shared with all the techniques aimed at analysing magma composition. The quantity of analysed chemical elements provides a large number of variables which can be worked with to characterize and differentiate each ignimbrite from the others. A low number of variables is a disadvantage of other techniques such as the magnetic methods (e.g. analysis of remanent magnetizations) or radiometric dating.

(2) *Independence of time span between ignimbrites emplacement*. In radiometric dating, to succeed in the differentiation of individual ignimbrites the separation in time of their emplacements must be larger than the precision of the dating method being used. In many occasions this is not the case. In the Sulcis, the ignimbrite sequence was emplaced over *c.* 3 Ma. This is one unit every 0.17 Ma on average, which is less than the best precision obtained on datings of this suite (±0.2 Ma using ^{40}Ar/^{39}Ar method in Pasci *et al.* 2001). The cost of radiometric dating also usually precludes the use of this technique when dealing with more than a few ignimbrites and areas to be correlated.

(3) *Not constrained by crystallization degree or mineral assemblage*. Applicability of whole-rock geochemistry is not constrained by the crystallization degree or mineral assemblage of the magma. Whole-rock analyses can be performed in samples ranging from glass (e.g. obsidian, aphyric vitrophyre) to holocrystalline material (e.g. some of the studied comenditic lava flows in the Sulcis). However, it must be taken into account (as mentioned in the Introduction and Methodology sections) that in pyroclastic deposits such as ignimbrites, heterogeneous deposition of glass shards, pumices and phenocrysts may introduce additional chemical variability to the deposit. Independence of crystallization degree and mineral assemblage is an advantage of whole-rock geochemistry when compared to another criterion such as the mineral chemistry of phenocrysts (e.g. Glazner *et al.* 1986; Shane, 1998; Harangi, Mason & Lukacs, 2005; Lebti *et al.* 2006; Jutzeler, Schmincke & Sumita, 2010; Aydar *et al.* 2012; Ellis *et al.* 2012; Sumita & Schmincke, 2013). Mafic minerals such as biotite or amphibole are regarded as the most useful phases for correlation (e.g. Harangi, Mason & Lukacs, 2005; Lebti *et al.* 2006) because of the larger chemical variability they may present compared to more simple phases such as

feldspars. However, ignimbrites in the Sulcis are mostly trachytic and rhyolitic in composition, presenting mineral assemblages largely dominated by feldspars. Mafic minerals are typically scarce, and frequently present preservation problems (they may be partly altered or show features that indicate instability; G. Gisbert, unpub. PhD thesis, University of Barcelona, 2012). The scarcity of appropriate mineral phases for correlation, combined with the chemical similarity of these phases between units, reduces the convenience of this method for the Sulcis area and probably also for other areas with strongly evolved volcanic rocks. In addition, even when the most appropriate mineral phases are present, chemical variation may be larger within a single thin-section than between ignimbrites (e.g. Glazner *et al.* 1986). Crystallization degrees and mineral assemblages are also issues for the radiometric dating methods, which typically use mineral separates instead of whole rock.

(4) *Not constrained by welding or consolidation degree of the studied deposits*. This is an advantage if compared to the analysis of glass or pumice separates, which need non-consolidated deposits or the existence of pumices which can be mechanically separated. In the Sulcis, most ignimbrites are strongly to extremely welded.

(5) *Obtained composition is already an average of the sample and is not affected by devitrification*. This point links with (4) above. The use of laser ablation techniques allows the analysis of single glass shards, which becomes extremely useful when pumices or shard separates cannot be obtained (e.g. in welded pyroclastic deposits). Laser ablation has therefore become one of the most popular techniques for obtaining magma compositions from pyroclastic deposits (both ignimbrites and tuffs), mainly for correlation purposes (e.g. Peate *et al.* 2003; Harangi, Mason & Lukacs, 2005; Suzuki *et al.* 2005; Pearce, Alloway & Westgate, 2008; Jutzeler, Schmincke & Sumita, 2010). However, analysis by laser ablation presents two main drawbacks. First, it can only be used when glass is preserved, a condition rarely met when studying old volcanic deposits in which alteration, diagenetic and even metamorphic processes have already acted on the studied materials (e.g. Orton, 1992). Devitrification may even occur during cooling or shortly after ignimbrite deposition, preferentially affecting non-welded facies (e.g. in the Sulcis; G. Gisbert, unpub. PhD thesis, University of Barcelona, 2012). Second, strong variability in shard composition has been found between shards in individual samples (e.g. Pearce, Alloway & Westgate, 2008; Santacroce *et al.* 2008). Santacroce *et al.* (2008) compared glass and whole-rock compositions from proximal pyroclastics of the Somma–Vesuvius and found that major-element variability was greater in glass shards than in whole-rock analyses. Pearce, Alloway & Westgate (2008) also found a great variability in trace element compositions, which was especially evident in the abundant trace elements (few hundred ppm) such as Ba, Zr and Rb. These elements showed variations between individual shards with standard deviations in the ±10–20 % range, which was far above the precision of LA-ICP-MS analyses for these elements (±2–3 %). The authors attributed this inter-shard variation to fractional crystallization and diffusion processes in the magma chamber. To take into account this variability multiple shard analyses are needed to correctly characterize a single rock sample, which increases the cost and time involved. Whole-rock analysis avoids these problems because the obtained geochemical composition of a sample is already an average; all that is needed is to remove any external bodies which could significantly modify the composition of the rock.

(6) *Usually accessible, fast and at moderate cost*. Whole-rock geochemistry analyses are usually accessible to most research centres at a cost which tends to be lower than other techniques (e.g. radiometric dating, laser ablation analysis, extensive electron microprobe characterization of glass and/or mineral phases from thin-sections, isotope ratios). In addition, large numbers of samples can be processed and data obtained in moderate amounts of time.

However, there are also drawbacks of whole-rock geochemistry, as described in the following.

(1) *Chemical heterogeneity of deposits*. Eruption, transport and deposition dynamics of ignimbrite deposits may introduce significant chemical heterogeneity (Walker, 1972; Hildreth & Mahood, 1985; Branney & Kokelaar, 1992, 2002; Orton, 1992). For example, compatible element contents will be higher in phenocryst-enriched portions of the deposit and lower in phenocryst-depleted portions; incompatible elements will have an opposite behaviour; a systematic sampling of each ignimbrite is therefore needed. A sufficiently large amount of samples require to be analysed so the whole geochemical variability of the ignimbrite is revealed. Any new sample may then be correctly attributed to the corresponding deposit. The number or required samples will vary according to the chemical variability of the studied ignimbrites or units (e.g. relatively homogeneous LE or PM units compared to chemically dispersed CF, NU or CO units in the Sulcis). In this study, an insufficient number of samples and good-quality analyses from CM and AC units implied that it was not possible to correctly characterize their chemistry.

(2) *Chemical zoning of the magma chamber*. Eruption of chemically zoned magma chambers producing chemically zoned ignimbrite deposits is common (e.g. P1 composite ignimbrite, Mogán Formation, Gran Canaria Island; Freund & Schmincke 1992, 1995; Freundt-Malecha, Schmincke & Freundt, 2001). The approach to follow when working with zoned ignimbrites is equivalent to that in the previous point. However, in suites with chemically zoned ignimbrites, wide chemical variability of each ignimbrite may produce chemical overlap between deposits, hamper their chemical differentiation, and render whole-rock geochemistry as a barely useful approach for unit correlation.

(3) *Chemical homogeneity of magmas in a volcanic suite*. If the magmas erupted in a given magmatic suite are too similar to each other, it may be impossible to chemically distinguish them (e.g. MC and CA units in the Sulcis).

These three issues also represent problems for the other mentioned correlation methods except for magnetic and radiometric methods, which are mostly independent of chemical compositions of magmas.

6.b. Usefulness of the methodology in the studied area

The methodology explained here for ignimbrite recognition and correlation proved to be a very useful tool in the Sulcis study area. Whole-rock geochemistry allowed us to correctly identify units forming specific outcrops and therefore solve doubts in unit correlation, including correlation of lithologically different facies belonging to the same unit.

The methodology presented here was especially useful for the identification of isolated samples. For example, one particular facies of the SP unit in NW Santo Antioco Island is rich in large enclaves of welded ignimbrite. Individual enclaves were analysed and investigated as unknown samples using the approach explained here. Results showed that these enclaves were in fact fragments of portions of the SP unit that were emplaced in earlier stages of the formation of this ignimbrite and had subsequently been cannibalized (brown lithic enclaves in SP unit; G. Gisbert, unpub. PhD thesis, University of Barcelona, 2012). As another example, the characterization of a small sample of an ignimbrite deposit recovered from a new prospective borehole drilled by the Carbosulcis SpA mining company in mainland Sulcis provided information on the stratigraphic position of the drilling front.

The methodology presented in this work was designed from, and to be used with, samples which yield high-quality analyses and exhibit few signs of alteration or weathering. However, identification of special samples is sometimes needed to solve specific stratigraphic or cartographic problems. The applicability of the provided diagrams to altered samples was investigated by including all the available analyses (fresh and altered samples) into the diagrams (not shown). It was found that most of the diagrams designed through observation of fresh samples are still of use when incorporating slightly altered rocks. It was therefore shown that the selection of the discriminating elements, with prioritization of immobile elements, was appropriate. As could be expected, the strongest modifications in whole-rock chemistry were observed in the least-welded rocks.

Considering the evidence provided in this work, we propose that whole-rock geochemical characterization of ignimbrite deposits is possible despite their natural heterogeneity, and that it can be used for ignimbrite deposit identification, both for academic and commercial purposes, not only in the Sulcis but probably also in other areas presenting ignimbrite stacks.

7. Conclusions

In this study the usefulness of whole-rock geochemical data for the characterization of ignimbrite deposits and as a tool for their correlation is shown through the study case of a Miocene ignimbrite sequence in the Sulcis area (SW Sardinia, Italy). Limitations and advantages of whole-rock geochemistry as a correlation tool compared to the most commonly used correlation techniques have been addressed in the provided example.

A protocol has been developed which allows the identification of most of the ignimbrite deposits in this area through the projection of whole-rock geochemical data into successive specially designed binary diagrams. This tool showed its usefulness as a complement to stratigraphic and lithologic criteria during the revision of the volcanostratigraphy and cartography of this study area.

The diagrams developed in this study can be used from now on by any researcher working in the Sulcis area to solve doubts in unit identification concerning this suite. Most importantly however, the methodology developed may be applied to other similar study areas containing several ignimbritic units or other volcanic deposits. As demonstrated in the provided example, in order to use identification diagrams with confidence in any study area a minimum amount of chemical data are needed to ensure that most of the chemical variability of each unit is represented. In addition, it is equally important to carefully select representative samples from each deposit and to remove any external bodies (e.g. accidental lithics) from samples before analysing their geochemistry.

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Declaration of Interests

None.

Supplementary material

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