Copper and arsenical copper artefacts from prenuragic Sardinian cultures

Giuliana Demurtas

Abstract

Due to its geographical position and numerous ore deposits, Sardinia played a significant, though still not completely defined, role in prehistoric metallurgy in the Mediterranean area. Up to now the most ancient metal production and working phases, where copper and the first alloy (copper-arsenic) were used, have not been documented archaeometrically, but only deduced from archaeological evidence. In this paper the results of the characterization of a first series of eleven finds (weapons) dating to the prenuragic era are presented. Analyses show five of the finds to be made of copper while the other six are arsenical copper with an arsenic content of up to 7%. Based on the microstructural characterization (SEM plus EDS and optical metallography), the possible ore provenance as well as the metal working techniques presumably used are discussed. The lead isotope composition of some of the weapons suggests that two arsenical copper swords of 'argaric' workmanship might have been made from Sardinian ores, while for a copper spearhead Cypriot-type ores might have been used.

Introduction

When addressing the question of archaeometallurgy in Sardinia, two periods can be conveniently distinguished, generically defined as 'prenuragic' and 'nuragic'. The prenuragic phase comprises the late Neolithic (Ozieri culture) and early Chalcolithic (Filigosu-Abealzu culture), around the end of the 4th millennium BC and continued through the whole of the Early Bronze Age (Bonnanaro A or Corona Moltana cultures) to around the beginning of the 2nd millennium. The cultural references of the prenuragic period are related to the succession of civilizations which inhabited the island while the chronologies are for the most part based on foreign cultures, with parallels in the types of metal artefacts and in metal production and working techniques. In fact, the metallurgy had spread far and wide crossing geographical and cultural boundaries, connecting, as far as is currently known, the entire eastern and western Mediterranean basin, including the east Atlantic coasts, regions of central Europe and the Near East[1-3]

The archaeologist Lo Schiavo argued, ten years ago[2] that:

> 'Investigations currently under way focus particular attention on metallurgy in that it is an index of the utmost importance for defining the technological level and the intercultural relationships of ancient peoples which provide information about social and economic organization of the greatest interest.'

After careful examination of the archaeological documentation available at the time 'for the entire delicate phase of its origins', the paper concludes with the following comment:

> 'In the light of these considerations, based on extremely interesting data that open up new research prospects, once again confirming the important place that Sardinia shows to have occupied in the ancient world, some question-marks and uncertainties do exist on given vital matters. This is due, unfortunately, to the inadequacy of the current system of approach and investigation: notably the lack of any kind of analysis: chemical, metallurgical, lead or other isotopes, carried out on the metal finds'.

By contrast, a great deal of data, though not exhaustive, has been published for the other Mediterranean regions, from the Iberian peninsula to the Near East[4-9]. The results indicate that certain aspects were common to the different cultures that developed these important early phases of metallurgy; for instance the arsenic content of the alloys varied over rather a narrow range. There is general consensus among scholars in this field that it was the very nature of the most common copper deposits that led to the first encounter with alloys. In fact these ore deposits typically contained a superficial layer with the sulphides weathered to oxides and carbonates and copper in the elemental state, underlying which were enrichment zones containing significant percentages not only of copper but also of arsenic, antimony, etc. Conversely, there are considerable differences of opinion as to whether the addition of arsenic to the alloy was deliberate, and concerning the smelting and forging techniques that would have improved the serviceability of the artefacts, in particular of weapons. Clearly there is a need to gain more knowledge of the finds belonging to this interesting phase in the development of metallurgy and also to reproduce the processes involved.

In this paper an attempt is made to fill a gap in the archaeometric documentation on Sardinia. Although numerous and complex ore bodies, presumably exploited since remote ages, are known, no archaeometric identification of early copper and arsenical copper objects has previously been undertaken.

Artefacts studied

The eleven finds studied here, provided by the Soprintendenza Archeologica in Sassari, are weapons unearthed from tombs during regular excavations or confiscated by the judicial authorities. They are briefly described below:

Small dagger with leaf-shaped blade, central rib and rectangular tang perforated at one end, 120mm long, from Su Monti, Orroli (NU)[2]

Two small laminar daggers with triangular blades from Murissiddi, Isili (NU), one having a very elongated shoulder with a hole at one end (No 5, 74mm long), and the other with a short tongue-like tang and two small holes on either side (No 6, 75mm long)[10]

Dagger with hooked tang (190mm long), site unknown (confiscated at Ottana, NU)[11]

Spearhead (277mm long), site unknown (confiscated at Ottana, NU)[11]

Sword of ‘argaric’ workmanship, belonging to the hoard of 19 weapons discovered in the so-called ‘Warriors’ Grave’ at Sant’Iroxi, in the commune of Decimoputzu (CA), labelled ‘SCH.497’. Archaeologists assume that originally the sword was 720mm long, 99mm wide with maximum thickness of about 4mm[12-13]

A second large ‘argaric’ broad-bladed flat sword with round tang and seven rivet-holes. Original length presumed to be about 600mm, from unknown locality in the commune of Maracalagonis (CA)[2] (Fig 1)

Dagger, 260mm long, with leaf-shaped blade, central rib and rectangular tang perforated at one end (Fig 2) unearthed at Janna Ventosa (NU)[2]

Three small daggers: one 75mm long with triangular blade and rounded shoulders with a hole on either side, discovered in the only settlement of the Bonnanaro culture known so far, at Sa Turricula di Muros (SS). Another two daggers, one 99mm long with tang (Fig 3), the other 79mm long with a trapeze shaped tang from Cave 1 at Frommosa a Villanovatulo (NU), associated with Bonnanaro material[14-15]

Analytical methods

Given the state of the finds, some of which were apparently well preserved while others were extremely thin and completely mineralized at the edges, it was not possible to take samples from all of them. Thus a

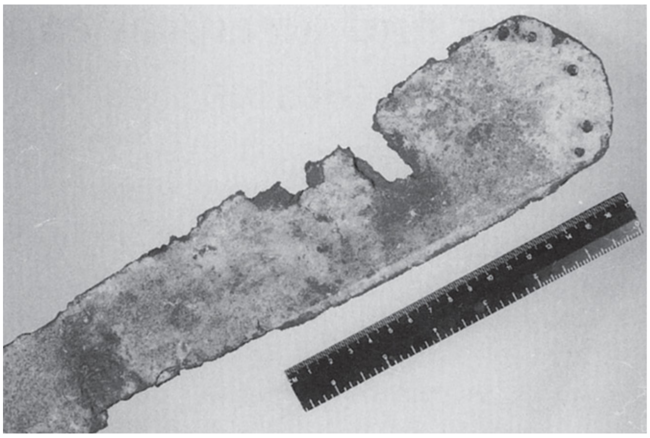

Figure 1: Sword from Maracalagonis.

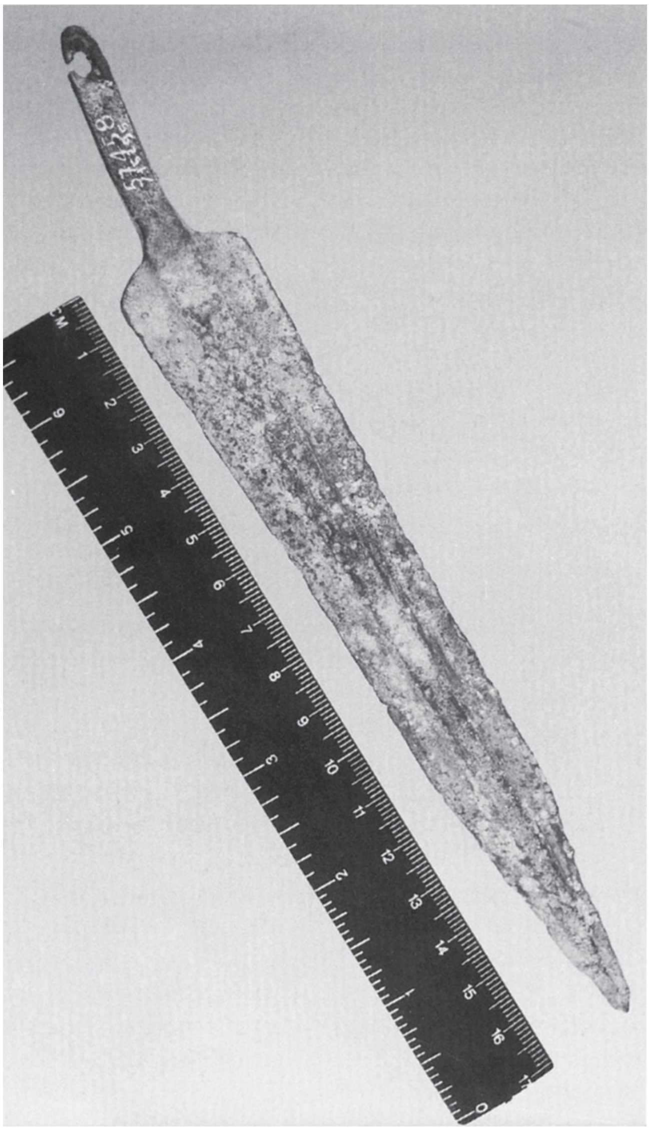

Figure 2: Dagger from Janna Ventosa.

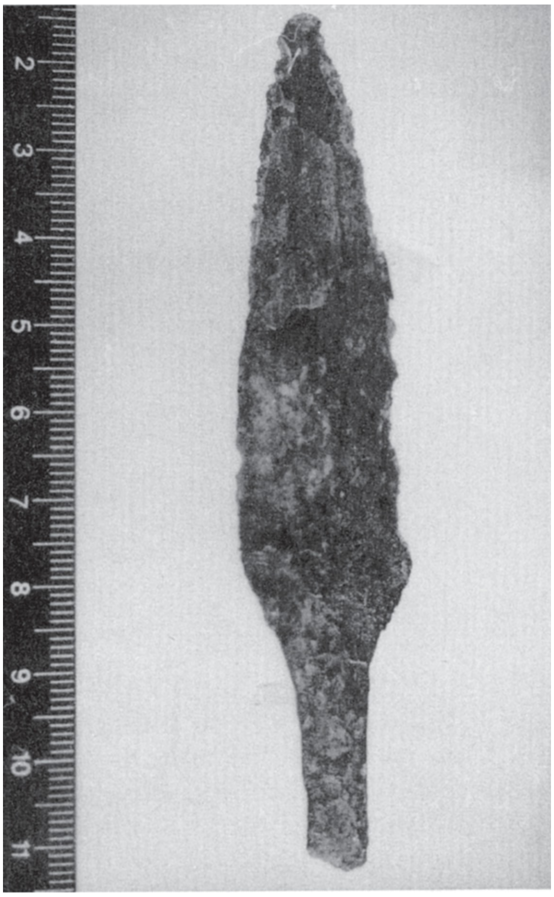

Figure 3: Dagger (No 8) from Frommosa.

preliminary non-destructive investigation was conducted by means of microanalyses under the scanning electron microscope (SEM), using energy dispersive spectrometry (EDS) for the purpose of determining, in semi-quantitative terms, the main alloy constituents. The analyses were performed after local patina removal using a lancet or a micromiller. It was only possible to remove samples for preparing metallographic sections from the Sant'Iroxi and Maracalagonis swords and from the spearhead from Ottana. The metallographic investigation on these sections was conducted under both the optical microscope and the SEM with EDS. Vickers microhardness was also measured under a load of 20gf.

Tin, iron, antimony, bismuth, cadmium, lead, zinc, nickel and silver were determined by means of atomic absorption spectrometry (AAS). This analysis was performed on those finds that could be cut, and on the dagger from Janna Ventosa from which a sample was removed by drilling along the rib (1mm diameter) and one of the Frommosa daggers.

The samples taken from the Sant'Iroxi and Maracalagonis swords as well as from the Ottana spearhead were sufficient to determine lead isotope compositions using ICP-MS; the standard ANSI 981 was referred to.

Results and Discussion

Table 1 shows the copper and arsenic contents of the weapons studied. It also indicates those finds for which it was possible to perform AAS, determine the lead isotope ratios and conduct metallographic investigations. The finds can be divided into two groups: some are composed of unalloyed copper, others of arsenical copper, with arsenic contents often varying from one point to another, up to a maximum of about 7%. In all cases tin was below detectable

Table 1: Semiquantitative surface analysis of the finds using EDS. The other analyses carried out are also shown.

Object	EDS analysis (wt%)			Other determinations		
	Cu	As	Sn	AAS	Lead isotope	Metallography
Su Monti dagger	100	-	-	-	-	-
Murissiddi dagger (No 5)	100	-	-	-	-	-
Murissiddi dagger (No 6)	100	-	-	-	-	-
Ottana dagger (No 12)	100	-	-	-	-	-
Ottana spearhead	100	-	-	yes	yes	yes
Sant'Iroxi sword	94-96	4-6	-	yes	yes	yes
Maracalagonis sword	96-97	3-4	-	yes	yes	yes
Janna Ventosa dagger	95-93	5-7	-	yes	-	-
Sa Turricola dagger	99-98	1-2	-	-	-	-
Frommosa dagger (No 8)	99-97	1-3	-	yes	-	-
Frommosa dagger (No 9)	98-93	2-7	-	-	-	-

Table 2: AAS analyses of trace elements (ppm).

Find	Sn	Pb	Bi	Sb	Fe	Zn	Ni	Ag
Ottana spearhead	nd	700	450	nd	600	10	nd	100
Sant'Iroxi sword	<6	4800	110	330	100	4	25	<0.04
Sant'Iroxi sword	<6	4700	90	280	10	4	10	10
Sant'Iroxi sword	<6	4700	140	330	30	4	30	4
Maracalagonis sword	nd	5600	170	1100	60	60	nd	20
Maracalagonis sword	nd	4300	170	1000	600	30	nd	-
Ventosa dagger (No 1)	nd	100	440	nd	330	30	80	900
Frommosa dagger (No 8)	nd	530	nd	nd	1500	20	nd	2000
Frommosa dagger (No 9)	nd	700	nd	nd	360	70	nd	300

nd = not detected. Cd <0.03 ppm, Sn <3 ppm, Sb <0.5 ppm, Bi <0.5 ppm, Ni <0.18 ppm.

levels (roughly 1%, under the experimental conditions used).

Table 2 shows the trace element analyses. These confirm that tin is present in extremely small amounts and thus always as an impurity and never as an alloy constituent. Generally speaking, only small percentages of iron were detected and this shows that the copper was not obtained from the chalcopyrite-type ores used by later civilizations and subjected to slagging, in some cases with the aid of iron ores. In these latter cases, even in the purer copper ingots such as oxhides, a much higher percentage of Fe has been found[16-19]. It is reasonable to suggest that the base metal used for the finds examined here was derived either from native copper or from the enrichment zones underlying the upper parts of the outcrops. The latter hypothesis is further reinforced in those cases where high trace levels of both antimony and bismuth are found, as these elements accompany copper in the course of the enrichment processes induced by weathering.

Lead is the trace element present in the greatest amounts. The highest amounts were observed in the two ‘argaric’ swords. This, together with their bismuth and antimony contents, suggests that the metal used for the two swords is from the same source. Only very small amounts of zinc, nickel and silver were detected in the finds, except for the Janna Ventosa dagger and the small dagger (No 8) from Frommosa which both contained significant amounts of silver. For the latter object it was possible to carry out two determinations which showed that the silver content of the dagger is not uniform.

The metallographic examination of three of the finds produced some interesting results. In particular, a number of inclusions was observed in the samples taken from the swords, elongated in the direction of hammering of the blades. These fall into the following three categories: copper associated with sulphur, copper associated with as much as 30% arsenic, and copper associated with both sulphur and arsenic in varying percentages (Fig 4). Clearly these are remnants of the minerals contained in the original ore such as tennantite ($Cu_3(As,Sb)S_3$) and enargite ($Cu_3As_3S_4$). The metallographic section of the spearhead from Ottana suffered from heavy intergranular corrosion.

Microhardness measurements yielded the following mean values: 154±12 kgf/mm^2 for the Sant’Iroxi sword and 137±15 kgf/mm^2 for the Maracalagonis sword. On average, these values are comparable to those reported in the literature for finds of similar composition[9,20]. These

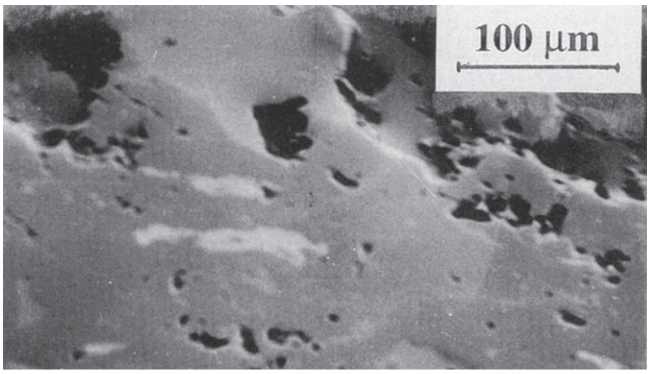

Figure 4: Sword from Sant’Iroxi, SEM image showing pale elongated inclusions containing arsenic, copper and sulphur.

results suggest that the blades' mechanical properties were adequate[21].

With regard to provenancing the metals, Table 3 gives the lead isotope data obtained. Considering comparable data currently available for the Mediterranean region[22-24], the two swords may be assumed to have similar provenance, compatible with the numerous mining districts of Sardinia, while the data for the copper spearhead are consistent with Cypriot-type ores.

Conclusions

These analyses have filled, at least in part, a gap in the documentation of archaeometallurgy in Sardinia. The finds dating to the prenuragic cultures can be divided into two groups which characterize the very first phases of metallurgy. Some are composed of pure copper while others are of arsenical copper. The arsenic content of the alloys varies from low levels, which may reasonably be assumed were obtained accidentally from ores in which minor amounts (a few percent) of arsenic occurred along with the copper minerals, to other objects where the higher arsenic contents (5-7%) are more probably the result of intentional alloying.

The metallographic investigation of the two swords showed numerous inclusions elongated in the direction of hammering, some containing significant amounts of arsenic and/or sulphur, relicts of the original ore. For these two swords the similarities in workmanship (defined as 'argaric' by the archaeologists) corresponds with the substantially similar alloy composition and microstructure. The two finds also have similar lead isotope compositions, which suggest a common source consistent with numerous Sardinian mining districts. On the other hand, the lead isotope data obtained for the spearhead are compatible with Cypriot-type ores. The latter finding, which clearly warrants further investigation with new data acquisition, suggests that a metallurgical connection existed between Sardinia and Cyprus much earlier than that documented for oxhide ingots, bronze tripods, etc in the subsequent Bronze Age.

Table 3: Lead isotope ratios (ICP-MS analyses).

Find	Pb^{208}/Pb^{206}	Pb^{207}/Pb^{206}	Pb^{206}/Pb^{204}
Sant'Iroxi sword	2.110	0.864	18.066
Sant'Iroxi sword	2.108	0.864	18.123
Sant'Iroxi sword	2.102	0.867	18.071
Maracalagonis sword	2.098	0.872	17.917
Ottana spearhead	2.081	0.842	18.473

Acknowledgements

This work has been carried out with the financial support of the Cultural Heritage Project of the Italian National Research Council, within the framework of the activities of the working group coordinated by Prof U Sanna. The archaeological finds were made available by the Soprintendenza Archeologica of Sassari and Nuoro, directed by F Lo Schiavo. Grateful thanks are due to G Ugas, the scientist in charge of the excavations at Sant'Iroxi and the competent archaeological authorities for the provinces of Cagliari and Oristano for providing a sample of the sword. The AAS analyses were done by A Viola of the Department of Chemical and Materials Engineering, and the ICPMS determinations by A Rivoldini of DIGITA. The views expressed are those of the author alone.

References

1. Webster G S, *A Prehistory of Sardinia* (Sheffield 1996), 72-77.
2. Lo Schiavo F, 'Le origini della metallurgia ed il problema della metallurgia nella cultura di Ozieri', in L Dettori Campus (ed) *La cultura di Ozieri. Problematiche e nuove acquisizioni* (Ozieri 1988), 284.
3. Lo Schiavo F, 'Nota a margine delle spade argariche trovate in Sardegna', *Quaderni della Soprintendenza Archeologica di Cagliari-Oristano* 8 (1991), 69-81.
4. Gale N H and Stos-Gale Z A, 'Some aspects of early Cycladic copper metallurgy', in C Domergue (ed) *Minieria Y Metallurgia en las Antiguas Civilizaciones Mediterraneas Y Europeas* (Madrid 1989), 21-35.
5. Balthazar J W , 'New Compositional and metallographic analyses of copper-base objects from Lapithos, Vrysi Tou Barba', *MASCA Journal* 4(2) 1986, 60-69.
6. Arribas A, Craddock P, Molina F, Rothenberg B and Hook D R, 'Investigation arqueo-metallurgica en yacimientos de las edades del cobre y del bronce en el sudeste de Iberia', in C Domergue (ed), *Minieria Y Metallurgia en las Antiguas Civilizaciones Mediterraneas Y Europeas* (Madrid 1989), 71-78.
7. Eaton E R and McKerrell H, 'Near Eastern alloying and some textual evidence for the early use of arsenical copper', *World Archaeology* 8(2) (1976), 169-191.
8. Rovira S, Montero I and Consuegra S, 'Archaeometallurgical Study of Palmela Arrow Heads and other Related Types', in E Antonacci Sanpaolo, *International Colloquium on Archaeometallurgy* (Bologna 1992), 270-289.
9. Caneva C, Frangipane M and Palmieri A, 'Scienza e tecnologia dei bronzi arsenicali di Aslantepe', in E Antonacci Sanpaolo, *International Colloquium on Archaeometallurgy* (Bologna 1992), 402-413.
10. Lo Schiavo F, personal comunication.
11. Lo Schiavo F, 'Compleso di armi di "bronzo" da Ottana', in F Lo Schiavo *Sardegna centro-orientale dal neolitico alla fine del mondo antico*, (Sassari 1978), 75-79.
12. Ugas G, *La tomba dei guerrieri di Decimoputzu* (Cagliari 1990).
13. Atzeni C, Demurtas G and Sanna U, 'Metallographic and

Microanalytic Characteristics of a Pre-Nuragic Cu-As Alloy Sword', *La Metallurgia Italiana*, 11/97 (1997), 35-41.
14. Ferrarese Ceruti M L, 'La cultura del Vaso Campaniforme - Il Primo Bronzo', *Ichnussa* 74 (1981), 15-24.
15. Lo Schiavo F, 'Sardinian Metallurgy: The archaeological background', in M S Balmuth (ed), *Studies in Sardinian Archaeology II. Sardinia in the Mediterranean* (Ann Arbor 1986), 236.
16. Lo Schiavo F, Maddin R, Merkel J, Muhly J D and Stech T, 'Analisi metallografiche e statistiche sui lingotti di rame della Sardegna', *Quaderni della Soprintendenza Archeologica delle Provincie di Sassari e Nuoro* 17 (1990), 1-227.
17. Gale N H and Stos-Gale Z A, 'Oxhide ingots from Sardinia, Crete and Cyprus and the Bronze Age Copper trade: new scientific evidence', in M S Balmuth (ed), *Studies in Sardinian Archaeology III. Nuragic Sardinia and the Mycenaean World* (Oxford 1987), 135-177.
18. Craddock P T and Meeks N D, 'Iron in ancient copper', *Archaeometry* 29 (1987), 187-204.
19. Tylecote R F, Ghaznavi H A and Boydell J, 'Partitioning of trace elements between the ores, fluxes, slags and metal during the smelting of copper', *Journal of Archaeological Science* 4 (1977), 305-333.
20. Maréchal J R, 'Le leghe di rame utilizzate nella metallurgia primitiva europea', *La Metallurgia Italiana* (1962), 22-32.
21. Tylecote R F, *A History of Metallurgy* (London 1976), 8.
22. Stos-Gale Z, Gale N H, Houghton J and Speakman R, 'Lead isotope data from the Isotrace Laboratory Oxford: *Archaeometry* data base 1, Ores from the western Mediterranean', *Archaeometry* 37(2), (1995), 407-415.
23. Stos-Gale Z A, Gale N H and Annetts N, 'Lead isotope data from the Isotrace Laboratory Oxford: *Archaeometry* data base 3, Ores from the Aegean, part 1', *Archaeometry* 38(2), (1996), 381-390.
24. Gale N H, Stos-Gale Z A, Maliotis G and Annetts N, 'Lead isotope data from Isotrace Laboratory Oxford: *Archaeometry* data base 4, Ores from Cyprus', *Archaeometry* 39(1), (1997), 237-246.

The author

Giuliana Demurtas has a degree in physics from the University of Cagliari and a PhD in metallurgy from the Polytechnic of Torino. Her research has been concerned primarily with ancient metallurgical techniques, and physical methods for microstructural characterization of prehistoric copper-based finds. She has published over ten papers in this field.

Address: Department of Chemical and Materials Engineering, University of Cagliari.