Regional variation in the crustal abundance of minor elements: evidence from the granites of Sardinia

A. HALL

Department of Geology, King's College, Strand, London, WC2R 2LS

SUMMARY. The granites of Sardinia have been analysed for copper, lead, and zinc, and each element has been found to show a regional variation. There is a close relationship between the copper and lead contents of the granites and the distribution of copper and lead mineralization in the island, but very little relation between the zinc contents of the granites and the distribution of zinc mineralization. This is attributed to a greater degree of lithophile character of zinc in the magmatic source region.

THERE are many indications that the earth's crust is not uniform in respect of its content of certain elements. Differences in the distribution of mineralization have given rise to the concept of metalliferous provinces, such as the tin-rich province of Cornwall, the copper-rich province of Arizona, or the lead–zinc-rich province of south-west Sardinia.

If, as many authors believe, granitic magmas originate in the crust, differences in crustal trace-element abundances should be reflected in the compositions of granites. With this in mind, an investigation has been made of the distribution of copper, lead, and zinc in the granites of Sardinia.

Sardinia (fig. 1) may be divided geologically into: Palaeozoic and perhaps Pre-cambrian sedimentary and metamorphic rocks; granites of late Palaeozoic (Variscan) age; and Mesozoic and Tertiary sedimentary and volcanic rocks. There is abundant mineralization, of which the most important economic deposits are those of lead and zinc, with less important deposits of copper and other metals. The mineralization is not uniformly distributed. The lead–zinc mineralization is strongly concentrated in the south-western part of the island, and is very poorly developed in the north-east. The reason for considering south-western Sardinia as a region in which the crust is rich in lead and zinc is that the mineralization has recurred frequently and is not confined to a single period or genetic type of deposit (Zuffardi, 1965, 1969). There are deposits ranging in age from Cambrian to Recent, formed by a wide variety of sedimentary, metamorphic, and hydrothermal processes. Copper mineralization is less intense and is comparatively uniformly distributed.

Sampling, analysis, results

The island was divided by a grid into 10-km squares, with the aim of collecting one sample per square. The samples were collected from the freshest available outcrop within each square and where more than one petrographic type was represented in a square each type was sampled. Ninety-six samples of granite were eventually collected,
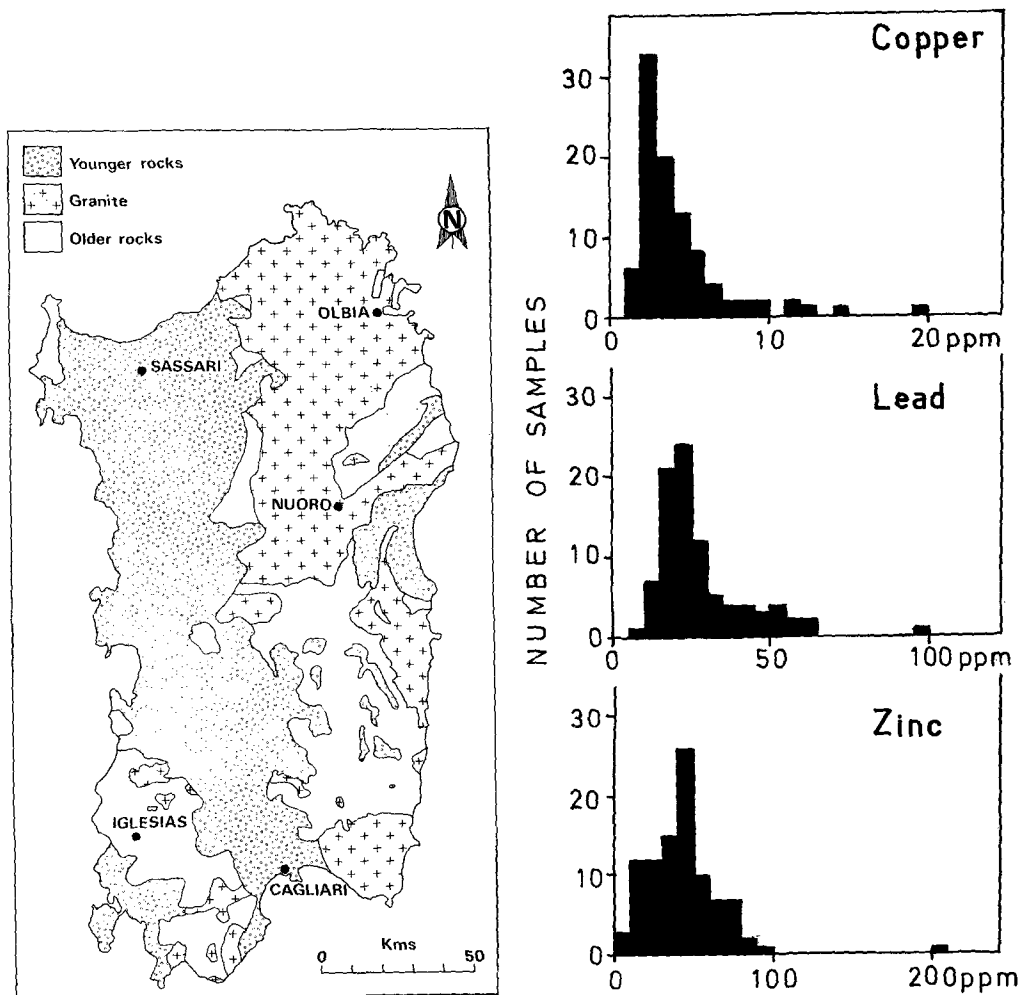
FIGS. 1 and 2: FIG. 1 (left). The distribution of granites in Sardinia. FIG. 2 (right). Copper, lead, and zinc contents of the 96 analysed samples of granite from Sardinia. Other lead concentrations found are 96, 135, 191, 259, 571, 764, and 831 ppm. One copper concentration was 129 ppm.

representing all the main intrusions in the island. In addition to copper, lead, and zinc, they have been analysed for calcium, iron, potassium, and rubidium to facilitate the interpretation of trace-element variation. Copper, lead, zinc, and iron were determined by atomic absorption spectrophotometry and calcium, potassium, and rubidium by X-ray fluorescence. The contents of Cu, Pb, and Zn are shown diagrammatically in Fig. 2. Concentrations of the other elements are in the ranges: Ca 0·17–3·29 %, Fe 0·57–4·24%, K 1·78–4·47%, Rb 66–394 ppm. A complete list of the analyses is available from the author on request.

Average concentrations. The ranges of concentrations of the trace elements are very large, with a small number of very high values for each element. The histograms in fig. 2 indicate highly skewed distributions for copper and lead. Examination of cumulative frequency diagrams (figs. 3 and 4) shows that the frequency distributions of copper and lead are nearer to lognormal than to normal and the distribution of
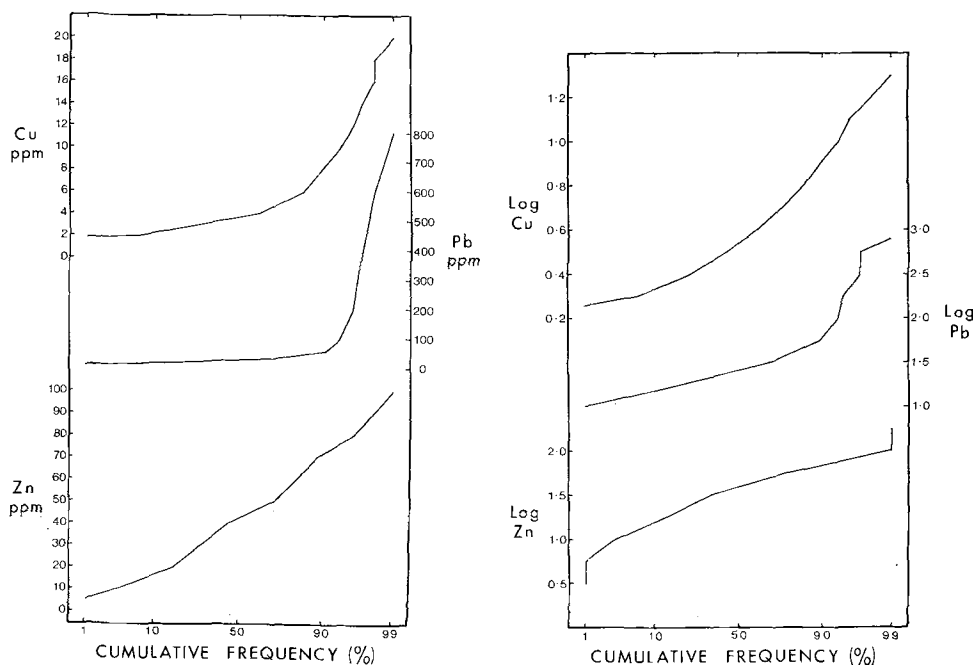
FIGS. 3 and 4: FIG. 3 (left). Cumulative frequency diagram for the Cu, Pb, and Zn contents of Sardinian granites. FIG. 4 (right). Cumulative frequency diagram for logarithms of the Cu, Pb, and Zn contents of Sardinian granites. Both diagrams have been plotted on normal probability paper: a straight line would correspond to a normal or lognormal distribution of the elements.

zinc is intermediate between normal and lognormal. None of the elements has a simple distribution; there is positive skewness even in the logarithmic distribution curves for copper and lead, as well as anomalously high values of all three elements. The large deviations of the frequency distributions from normality necessitate the use of distribution-free methods in the subsequent statistical examination of the results.

In comparison with the granites of other areas, the Sardinian granites are very poor in copper, rich in lead, and rather poor in zinc, as can be seen in Table I. The comparison is complicated by the asymmetrical frequency distributions of copper and lead. The positively skewed copper distribution (mean > median) is common to several of the other regions quoted in Table I, and there is no reason to doubt the Cu-poor character of Sardinian granites, but the distribution of lead is not

usually so asymmetrical. The data given by Mantei *et al.* (1970) for the Marysville stock indicate a mean lead content of 26 ppm (less than half that of Sardinian granites) but a median lead content of 23 ppm (nearly the same as that of Sardinian granites). The granites of the Sierra Nevada batholith, like those of Sardinia, have a median lead content between 20 and 30 ppm (Dodge, 1972), but the mean value is 20 ppm

TABLE I. *Mean copper, lead, and zinc contents of Sardinian and other granites (ppm)*

	Cu	Pb	Zn	Reference
Sardinian granites (96)	6	54	43	—
All granitic rocks	20	17	50	Turekian and Wedepohl (1961)
Sierra Nevada (545)	20	20	—	Dodge (1972)
N. Portugal (16)	16	19	—	Albuquerque (1971)
Marysville (89–90)	13	26	61	Mantei et al. (1970)
Galway (127)	25	56	66	Coats and Wilson (1971)
N. Tien Shan (48–9)	—	30	53	Zlobin et al. (1965)
Susamyr (76–80)	—	25	56	Zlobin et al. (1965)
Cape Province (34)	8	31	—	Kolbe and Taylor (1966)
Snowy Mts. (32)	17	28	—	Kolbe and Taylor (1966)
New England, N.S.W. (117)	7	20	—	Flinter et al. (1972)
Yukon (> 100)	10	35	64	Garrett (1972)
Sardinian granites (MEDIAN)	3	24	42	—

The number of analysed samples is given in brackets.

TABLE II. *Correlation coefficients (Spearman's r) between various pairs of elements in Sardinian granites*

Positive correlations

Ca–Fe	Zn–Fe	Zn–Ca	Cu–Fe	Cu–Zn	K–Rb/K	Cu–Ca	Pb–K	Pb–Rb/K
0·938	0·838	0·743	0·524	0·499	0·460	0·451	0·391	0·298

Negative correlations

Ca–K	Fe–K	Zn–K	Ca–Rb/K	Fe–Rb/K	Pb–Ca	Zn–Rb/K	Cu–K	Pb–Fe	Pb–Zn	Cu–Rb/K
−0·881	−0·793	−0·646	−0·552	−0·481	−0·364	−0·353	−0·326	−0·281	−0·231	−0·223

The correlation coefficient for the pair Cu–Pb is 0·086, which is below the limit of significance at the 95 % confidence level (±0·201 for a sample of 96).

for the Sierra Nevada granites compared with 54 ppm for Sardinian granites. Only a minority of the Sardinian samples attain lead contents that are exceptional by comparison with other areas.

Inter-element correlations. Copper, lead, and zinc values have been examined for correlation between them, or between them and the other elements analysed. Because of the deviations from normality of the frequency distributions, Spearman's distribution-free rank correlation coefficient (r) was used to test the correlations (Snedecor and Cochran, 1967). The results are given in Table II.

Copper and zinc show a strong positive correlation with each other and with iron and calcium. The interpretation is that entry of these elements into the magmas was controlled by isomorphous substitution for iron in ferromagnesian minerals during the

processes of magma formation and evolution. The correlation with calcium is a conse-
quence of the similar variation of calcium and iron, both of which are mainly contained
in minerals with high melting temperatures. The small number of specimens with
extremely high values of Cu and Zn do not have proportionately high Fe contents,
suggesting that very high values are determined by a process other than isomorphous
substitution for iron.

Lead shows a positive correlation with potassium, but a negative correlation with
calcium and iron. This is to be expected, since lead is known to be able to substitute
isomorphously for potassium, and potassium varies inversely with calcium and iron.
However, the correlation of lead with potassium is rather weak, and the high values
of lead can not be accounted for by this mechanism; the lead-rich samples include
ones with both high and low potassium contents.

Lead and copper are predominantly chalcophile elements and are preferentially
held by the sulphide phases in rocks. Their correlation with K and Fe may indicate
a shortage of sulphide minerals in the magmatic source region. Zinc can display
either chalcophile or lithophile character, and its very strong correlation with iron
indicates that lithophile behaviour has predominated during the development of the
magmas, again possibly indicating a shortage of sulphur during the development of
the magmas.

The negative correlation between lead and zinc is especially noteworthy, since it is
in marked contrast to the close association of these elements in the Sardinian ore
deposits. The difference is presumed to reflect the different geochemical behaviour
of the two elements under reducing and oxidizing conditions (Smith, 1963). Under
reducing sedimentary conditions, in the presence of sulphide ions, the chalcophile
property of zinc predominates and both lead and zinc form closely associated sul-
phide minerals. Under less reducing conditions the lithophile character of zinc pre-
dominates, and it is held by acid igneous rocks mainly in isomorphous substitution
for iron in ferromagnesian minerals, whereas lead retains a preference for precipita-
tion as sulphides, or enters potassium minerals isomorphously in small amounts if
there is no sulphide available. The association between lead and zinc in the Sardinian
mineral deposits is therefore a consequence of sedimentary processes of concentra-
tion, and a similar association in the granitic rocks is not necessarily to be expected.

Regional trends

Trend-surface analysis has been used to measure regional variation in the base-
metal contents of the granites. Conventional trend-surface analysis is not immediately
applicable to the Sardinian base-metal data because of their very asymmetrical
frequency distributions. Trend surfaces calculated from the raw data do not have the
normal distribution of residuals required for the valid application of the technique. It
is therefore impossible to calculate surfaces that show how the *mean* content of each
trace element varies from place to place. It is, however, possible to calculate median
surfaces, which show the variation in the *median* content of each element in different
areas. The calculation of median surfaces has been described elsewhere (Hall, 1973a),
and the details will be only briefly mentioned here.

The procedure was as follows: The data for each element were ranked, and polynomial regression surfaces of first to sixth degree calculated (O'Leary *et al.*, 1966) using the ranks as the dependent variable. Normality tests were applied to the residuals, and analysis of variance was used to assess which degree of surface fitted the ranks best in each case. No significant skewness of the residuals was found, indicating compliance with the main requirement of the median surface model. The analysis of variance showed significant contributions to the fit of the regression surfaces (at the
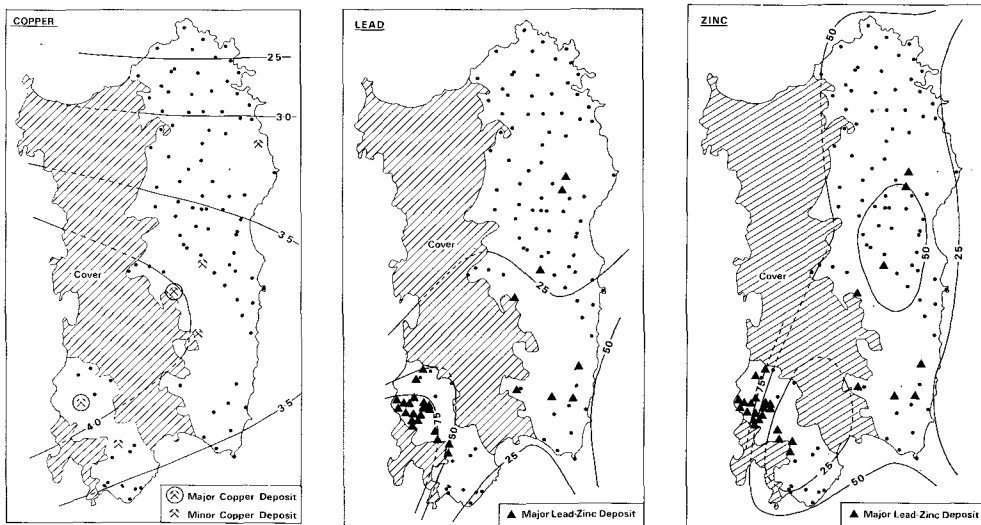
FIGS. 5 to 7: FIG. 5 (left). Median surface showing the regional variation in median copper content of Sardinian granites (in ppm). The localities of known Cu deposits are from Zuffardi (1965). FIG. 6 (middle). Median surface showing the regional variation in median lead content of Sardinian granites (in ppm). The localities of Pb–Zn deposits are from Zuffardi (1965). FIG. 7 (right). Median surface showing the regional variation in median zinc content of Sardinian granites (in ppm). The localities of Pb–Zn deposits are from Zuffardi (1965).

90 % confidence level) by components of up to the 2nd degree for copper, the 3rd degree for lead, and the 4th degree for zinc. The rank surfaces of these degrees were therefore detransformed into the original units (ppm), giving the median surfaces shown in figs. 5, 6, and 7 respectively.

To compare the trends of base-metal content of the granites with occurrences of mineralization, all the known mineral deposits are shown in figs. 5 to 7, but the occurrences of lead and zinc in Sardinian ore deposits are so closely related that the two can not be separated, and the lead–zinc deposits are shown together in figs. 6 and 7.

The copper levels in the granites only vary between about 2 and 5 ppm in fig. 5. The island's two major copper deposits both lie in the area of highest copper content of the granites, and the minor copper deposits are mostly in or near this area.

The granites show a much greater range of lead than of copper contents, and the

highest contents are found towards the south-west and south-east corners of the island, especially the south-west. By far the most intense lead–zinc mineralization is found in the Iglesias area of south-western Sardinia, precisely where the lead values for the granites are highest. Lead mineralization also occurs near the area of high lead values in south-eastern Sardinia, but there are also a few deposits in areas where the values are much lower. There is obviously a close relationship between the lead contents of the granites and the distribution of mineralization.

The zinc trend also shows a wide range, with highest levels being in south-western Sardinia (Iglesias district) and in the east-central part of the island. This distribution is definitely dissimilar to that of lead: the high zinc area in east-central Sardinia corresponds to an area of low lead values, while the high lead area of south-eastern Sardinia corresponds to one of very low zinc content. The distribution of zinc mineralization is the same as that of lead, but some of the most important deposits are in an area of south-western Sardinia (Rosas–M. Tamara) where the content of zinc in the granites drops to its lowest level. There is thus no direct relationship between the amount of zinc in the granites and the presence of zinc mineralization, in contrast to the relationship observed for the other two elements.

Petrogenetic implications

The trace-element contents of the igneous rocks in any particular area are determined initially by the geochemistry of the magmatic source region, and may subsequently be modified by differentiation or contamination during ascent and emplacement of the magmas.

Differentiation and contamination. In so far as the ranges of Ca, Fe, and K contents may denote a degree of contamination or differentiation of the magmas, a similar amount of variation in the base-metal contents may also be attributed to these mechanisms. The trace-element variations are much more extreme than the major-element variations, however, especially those of Cu and Pb, as well as having different types of frequency distribution, and these features are not explicable by either mechanism.

The lead content is the only one whose correlation with the major elements is compatible with enrichment in low-melting magma fractions, and to bring about its very high concentrations an extreme degree of fractionation would be required. The Rb/K ratios, which may be expected to rise with progressive fractionation, provide no evidence that the high lead contents are due to extreme fractionation. The correlation of Pb with Rb/K (Table II), although positive, is no greater than the correlation of Pb with K, and no more than would be expected from the association of Pb and K. In the samples from south-western Sardinia, where the trend of lead content is highest, or in the ten individual samples with highest lead content, the correlation of Pb with Rb/K is not high enough to be statistically significant (Table III).

In general, contamination by country rocks would result in the granites acquiring higher Ca and Fe and lower K contents than their original magmas. The correlations of lead with these elements (Table II) rule out the likelihood that the high Pb contents are due to contamination. Contamination might be expected to give rise to relatively

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high Cu and Zn contents, but in the samples with the highest Cu content there is no positive correlation of Cu with Fe and Ca, and in the samples with the highest Zn there is no correlation of Zn with Fe and Ca (Table III), indicating that the highest concentrations of these elements are not due to contamination. Furthermore in neither the most Cu-rich nor the most Zn-rich samples is there a positive correlation between Cu and Zn, which suggests that the granites have not acquired their highest

TABLE III. *Correlation coefficients (Spearman's r) between* Cu, Pb, Zn, *and other elements in selected groups of samples of granite*

	The 14 samples from SW. Sardinia (Iglesiente-Sulcis)		The 10 samples with the highest Cu content		The 10 samples with the highest Pb content		The 10 samples with the highest Zn content	
Positive correlation	None		Zn–Fe	0·779	Cu–Zn	0·894	None	
			Pb–K	0·655	Zn–Fe	0·858		
			—	—	Cu–Fe	0·685		
No significant correlation (at 95 % confidence level)	Zn–Fe	0·512	Zn–Ca	0·621	Zn–Ca	0·585	Pb–K	0·555
	Cu–Zn	0·419	Cu–Pb	0·618	Pb–K	0·536	Cu–Fe	0·479
	Pb–Fe	0·362	Cu–K	0·552	Pb–Rb/K	0·482	Cu–Ca	0·403
	Cu–Pb	0·338	Zn–Rb/K	0·082	Cu–Ca	0·345	Cu–Pb	0·215
	Zn–Ca	0·275	Pb–Zn	−0·115	Cu–Pb	−0·179	Zn–K	0·039
	Pb–Ca	0·274	Cu–Rb/K	−0·152	Cu–K	−0·188	Zn–Ca	−0·045
	Pb–Zn	0·177	Pb–Rb/K	−0·230	Pb–Zn	−0·230	Pb–Zn	−0·076
	Cu–K	0·011	Cu–Ca	−0·479	Pb–Fe	−0·330	Cu–K	−0·079
	Cu–Fe	−0·021	Cu–Zn	−0·494	Zn–K	−0·373	Zn–Fe	−0·094
	Cu–Ca	−0·111	Pb–Fe	−0·552	Pb–Ca	−0·439	Cu–Zn	−0·173
	Pb–K	−0·111	Cu–Fe	−0·612	Cu–Rb/K	−0·527	Pb–Fe	−0·221
	Zn–K	−0·284	Zn–K	−0·615	Zn–Rb/K	−0·627	Cu–Rb/K	−0·236
	Pb–Rb/K	−0·335	Pb–Ca	−0·636	—	—	Zn–Rb/K	−0·361
	—	—	—	—	—	—	Pb–Ca	−0·421
	—	—	—	—	—	—	Pb–Rb/K	−0·433
Negative correlation	Cu–Rb/K	−0·540	None		None		None	
	Zn–Rb/K	−0·640						

For a sample of 14, there is a significant correlation at the 95 % confidence level if $r > 0.532$ or $< −0.532$; for a sample of 10, the limits are $r > 0.648$ or $< −0.648$.

concentrations of these elements from the same source. South-west Sardinia is a special case in that much of the Pb–Zn mineralization of the country rocks, a potential source of serious contamination, occurs in limestones, and the effects of contamination should be reflected in the correlations with calcium. In fact there is no significant correlation between any of the base metals and calcium in the samples from south-western Sardinia (Table III). The minimum zinc concentration in the trend-surface map (fig. 7) is in an area of south-western Sardinia where there are important zinc deposits in the country rocks, while high zinc contents occur in the central-eastern part of the island where there is not much mineralization in the country rocks.

The major variations in Cu, Pb, and Zn are therefore considered to originate in the magmatic source region, rather than being attributable to contamination or differentiation.

The magmatic source region. It is assumed that the Sardinian granite magmas originated by partial melting in the crust. This assumption is based on three lines of

evidence: the great preponderance of acid over basic material in the Variscan magmatism of Sardinia (Ghezzo *et al.*, 1972); the relationship between magma compositions and geothermal gradients in the Variscan orogenic belt as a whole (Hall, 1973b); and the high initial $^{87}Sr/^{86}Sr$ ratios (0·709) in Sardinian granites (Del Moro *et al.*, 1972).

The evidence of mineralization suggests that the crust in this region is richest in Pb and Zn in the south-west of the island, whereas Cu is comparatively uniformly distributed. As far as Cu and Pb are concerned, this corresponds to the trends that are observed in the trace–element contents of the granites, but this is not the case for Zn. This discrepancy can be explained by the difference in behaviour in the magmatic source region between those trace elements that enter the minimum-melting liquid and those that tend to remain in the unmelted residuum. Copper and lead may be expected to belong to the first category, and zinc to the second category. Copper and lead, as chalcophile elements not substituting easily in silicates, would readily enter granitic magmas formed by partial melting. Zinc, on the other hand, having a greater degree of lithophile character, might or might not enter the melt. In areas where the source rocks were relatively poor in sulphides the zinc would mostly be held by ferromagnesian silicates, and remain in the residuum on partial melting. Thus zinc-rich areas of the crust would not necessarily give rise to zinc-rich magmas on melting.

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