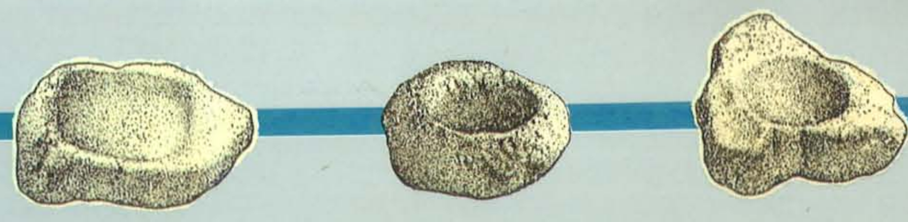
A. RAMOS-MILLÁN • Mª A. BUSTILLO (Eds.)

SILICEOUS ROCKS AND CULTURE



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Geochemistry of Radiolarites from the Betic Cordillera: Implications for Source Determination of Raw Material in Archaeology

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Resumen

En el presente trabajo se lleva a cabo un estudio petrológico y geoquímico de las radiolaritas jurásicas existentes en la Zona Subbética de las Cordilleras Béticas. El objetivo es establecer las diferencias entre las diferentes columnas estudiadas (AB, AG, SP, JH, SE y ZG) con vistas a su utilización como criterio diferenciador para estudiar las fuentes de suministro de los artefactos líticos encontrados en esta zona. Los niveles de radiolaritas están compuestos principalmente de cuarzo (50%-80%) y cantidades variables de otros componentes: calcita (<30%), minerales de la arcilla (esmectita, illita y, ocasionalmente, kaolinita) (10%-35%) y hematites (<5%). El análisis de los elementos mayores, menores, trazas y tierras raras es el mejor método para separar los diferentes niveles de radiolaritas estudiados. De acuerdo con esto, la sílice biogénica y total nos permite establecer dos grandes grupos: (1) las columnas AB y AG y (2) las columnas ZG, SP y JH, mientras que la columna SE no queda bien definida. En el primer grupo (<64% de sílice biogénica), las columnas AB y AG se diferencian entre sí al comparar el porcentaje de sílice biogénica con el porcentaje de CaO. Así, las muestras pertenecientes a AG se adaptan a la recta de regresión obtenida mientras que las correspondientes AB quedan alejadas de dicha recta de regresión. Además, las muestras de la columna AB se caracterizan por unos valores concretos de los índices CE/CE y Lu_n/La_n. En cuanto al segundo grupo (<61% de sílice biogénica), las muestras correspondientes a SP y JH quedan claramente definidas al obtener la recta de regresión correspondiente al par de variables Al_2O_3 y K_2O.*
Palabras clave: *RADIOLARITA, GEOQUIMICA, JURASICO, CORDILLERAS BETICAS, DETERMINACION DE FUENTES.*

Abstract

In the Betic Cordillera (Subbetic Zone) radiolarian bearing sequences of the Middle to Late Jurassic age have been studied from a petrological and geochemical point of view. The objective of this paper is to establish the differentiating characteristics among the six chosen sections (AB, AG, SP, JH, SE and ZG) to use them as criteria for determination sources of the archaeological artefacts found in this area. The radiolarite beds are largely composed of quartz (50%-80%), with lesser amounts of calcite (<30%), clay minerals (smectite, illite and ocasionally kaolinite) (10% to 35%) and hematites (<5%). Analysis of major, minor, trace and rare earth elements is the best method to separate radiolarites among the studied sections. According to this, biogenic and total silica let us define two groups of sections: (a) AB and AG, and (b) ZG, SP and JH, and the SE section is not clearly defined. In the first group, AG and AB sections differentiate themselves when the percentage of biogenic silica (greater than 64%) is compared to the percentage of CaO. The AG samples adapt themselves to a typical regression line, and the AB samples are distant from the regression line. Furthermore the samples of the AB section clearly characterize themselves by Ce/Ce* and Lu_n/La_n indexes. In relation to the second group (<61% of biogenic silica), the samples from the SP and JH sections are defined by a typical regression line when the percentage of biogenic silica is compared to the percentage of Al_2O_3 or K_2O.
Keywords: RADIOLARITE, GEOCHEMISTRY, JURASSIC, BETIC CORDILLERA, SOURCE DETERMINATION.

Introduction

In the Betic Cordillera (Subbetic zone) radiolarian bearing sequences of the Middle and Late Jurassic age have been refered to as radiolarites in regional tectonic and stratigraphic papers, although, in a strict sense, the radiolarite presence (rocks where the amount of silica being more than 90%) is scarce. The majority of the cases are calcareous or argillaceous rocks, that have between 20% and 80% of radiolarians. After a general sedimentological, petrological and geochemical study, incorporating seven sections of the Radiolarite Sequence in the Middle Subbetic, Ruiz Ortiz *et alii* (1989) define four different types of pelagic rocks: radiolarite, siliceous mudstone, siliceous marl and limestones containing radiolarians. They consider radiolarites those rocks which possess more than 50% of biogenic silica.

The objective of this paper is to analyse the chemical composition of the radiolarites present in each section studied by the above mentioned authors (fig. 1). In this study, we will try to establish the differentiating characteristics between each section. These characteristics will be related to the mineralogical composition of the rocks and to their geological settings. With all of this data, the base will be formed for establishing sources of the arqueological artefacts found in this area. Similar works, from a geochemical point of view, have been published before by other authors (Sieveking *et alii* 1970, Aspinall and Feather 1972, Bruin *et alii* 1972, Craddock *et alii* 1983, among others).

The amounts of major elements have been chosen from the published data (Ruiz Ortiz *et alii* 1989) and they were analysed by X-Ray Fluorescence Spectroscopy. The trace and rare earth elements have been obtained by I.C.P.

Geological setting

The Betic Cordilleras are traditionally divided into an External zone in the north and an internal zone in the south. The External zone is subdivided into a Prebetic and Subbetic district. The subbetic presents rocks with ages ranging from Trias to Miocene, principally sedimentary, although some volcanic rocks are also present.

The typical Jurassic stratigraphic sequence of the middle Subbetic begins with shallow water shelf limestone and dolostone of the early Liassic age, which are overlaid sucessively by (1) limestone-marls rhytmites and marly "ammonitico rosso" of the late Liassic age; (2) a radiolarite sequence, which may locally be underlain by submarine volcanic rocks; and (3) carbonate turbidites of the late Jurassic age.

The "radiolarites" are generally Bajocian and Kimmerdgian, and generally there are two episodes of radiolarian rich sedimentation, separated by a phase of pelagic carbonate deposition. The radiolarite sequence thickness ranges from 25 to 230 m, with an average of 90 m. Within this sequence very different lithologies are located, the presence of marls and limestones with radiolarians is common.

The radiolarite beds studied are situated in different geological environments and sections (fig. 1). In section ZG and SE the radiolarite sequence overlies the "ammonitico rosso" facies, but in JH and locally in AG, this radiolarite sequence directly overlies submarine volcanic rocks.

Mineralogy and petrology

By X-Ray diffraction it was determined that the radiolarite beds are largely composed of quartz (between 50 and 80%) with lesser amounts of calcite (less than 30%), clay minerals (smectite, illite and ocasionally kaolinite) (between 10% and 35%) and hematite (less than 5%). The mineralogical data has been obtained by combining the semiquantitative amounts gathered through XRD analysis with the normative amounts considering the general chemical composition.

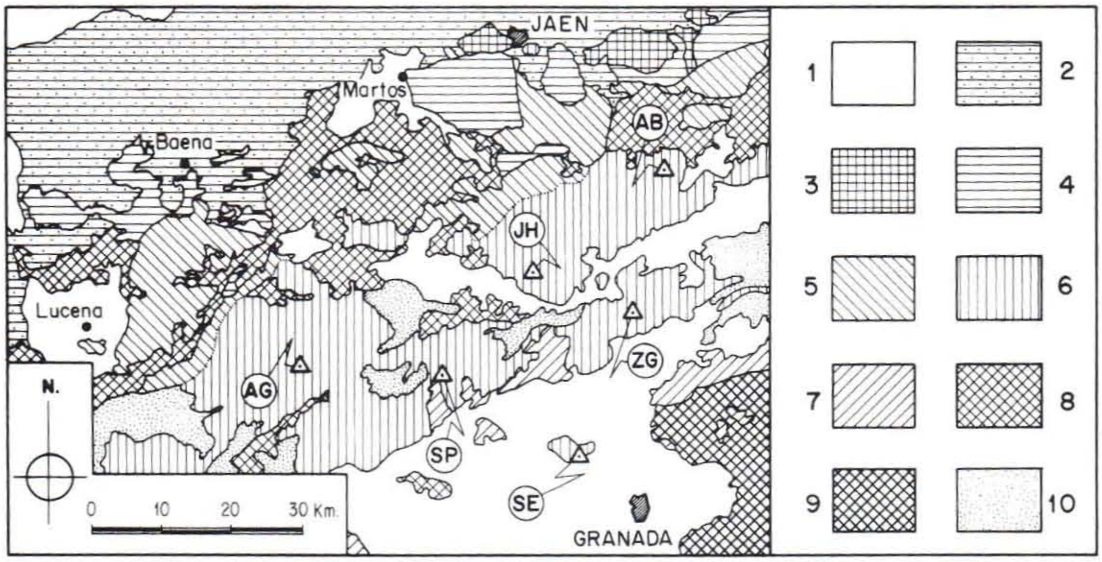

Figure 1.—Geological map including the position of the studied sections. 1. Neogene and Quaternary, 2. Olistotromes of the Guadalquivir basin, 3. Prebetic Zone, 4. Intermediate Units between the Prebetic and the Subbetic Zone, 5. External Subbetic Zone, 6. Middle Subbetic Zone, 7. Internal Subbetic Zone, 8. Triassic rocks, 9. Internal Zones and 10. Paleogene and/or Campo de Gibraltar Units. (Modified from Ruiz Ortiz *et alii,* 1989).

Using exclusively XRD analysis to obtain the mineral quantity that is found in proportions of less than 10% is not exact enough.

Projecting amounts of the main mineralogical components (quartz, calcite and clay minerals) on a triangular diagram (fig. 2), one can observe that it is difficult to establish differentiating mineralogical characteristics in each section, although general tendencies do exist. Of the three main components, calcite is the one which has a certain discriminative value. Using the calcite quantity as the criterion, the radiolarites of the SE section can be defined, although some of them will mix with the radiolarites of the JH section.

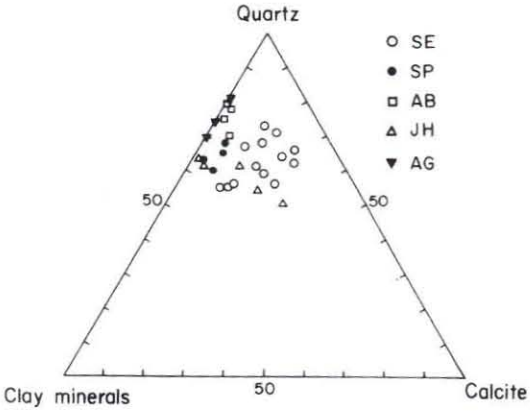

Figure 2.—Quartz-Clay Minerals-Calcite ternary diagram of the radiolarite beds in the different sections.

By thin section, the radiolarites present different levels of conservation. Sometimes, the radiolarians are well preserved and the rock shows packstone-wackestone texture. The radiolarian tests are filled with microcrystalline quartz and length-fast chalcedony. Sometimes diagenetic processes produce a redistribution of carbonate, silica and Fe-oxides and it is possible to see calcitized or oxidized radiolarians. On the other hand the silica released from the radiolarians is accumulated in determined places and very rich silica (quartz) zones are formed in the actual radiolarite beds.

In other cases the radiolarians show deformation and present ovoidal and flattened forms due to compaction. In some cases the radiolarians are practically unobservable and then crypto and microcrystalline quartz, micrite, clay minerals and Fe-oxides may come together to form a microcrystalline or criptocrystalline rock.

Geochemistry

Major elements

The composition of the rocks defined as radiolarites by Ruiz Ortiz *et alii* (1989) are shown in table I. According to these values it can be seen that the radiolarites richer in silica are found in AG and AB sections. Since the SiO_2 is the predominant constituent of the radiolarites, the authors normally characterize the radiolarites through variations in the nonsilica components (Al_2O_3, CaO, K_2O, etc.) by ratios of their concentrations rather than by their absolute concentration.

The main elemental relationships considered by the authors (Steinberg and Marin 1978, Barret 1981, Baltuck 1982, Hein *et alii* 1983, among others) for their interpretative value from the petrological and sedimentological point of view, are the following: Al/(Al+Fe+Mn), Si/(Si+Al+Fe), Si/(Si+Al-Fe-Ca), Fe/Ti and Fe/Al. In the radiolarites studied, these elemental relationships are not useful in discriminating given sections because it is frequent to find values that are superimposed in each section (fig. 3). Due to this aspect, the present study has been attempted to find new comparison parameters.

Table 1.—Major element composition in studied samples.

	SE-2	*SE-3*	*SE-4*	*SE-6*	*SE-9*	*SE-14*
SiO_2	74.00	77.00	70.02	64.50	67.13	76.62
Al_2O_3	2.76	3.08	5.21	2.70	2.45	5.21
MnO	0.15	0.19	0.14	0.25	0.32	0.15
MgO	1.40	1.00	1.11	1.10	1.67	2.01
CaO	8.80	6.89	9.14	13.47	12.50	6.44
Na_2O	0.31	0.17	0.25	0.26	0.43	0.33
K_2O	0.24	0.30	0.75	0.33	0.31	0.37
TiO_2	0.11	0.10	0.16	0.11	0.11	0.27
P_2O_5	0.02	0.01	0.04	0.05	0.03	0.11
Fe_2O_3	3.02	3.03	2.92	3.09	4.27	4.39
L.O.I.	9.13	7.71	10.18	13.95	10.84	7.71
B.S.6	67	69	57	57	61	64

	SE-15	*SE-21*	*SE-22*	*SE-37*	*SE-56*	*SE-68A*	*SE-68B*
SiO_2	69.58	70.80	64.60	71.79	72.66	69.97	70.80
Al_2O_3	3.07	7.41	4.60	7.84	3.98	4.91	7.13
MnO	0.20	0.09	0.21	0.06	0.20	0.22	0.20
MgO	1.11	0.77	0.89	1.15	1.22	0.65	0.93
CaO	11.65	6.92	13.01	5.87	7.93	10.87	7.06
Na_2O	0.30	0.20	0.11	0.15	0.25	0.13	0.18
K_2O	0.37	0.99	0.32	1.11	0.40	0.52	0.12
TiO_2	0.14	0.22	0.10	0.28	0.17	0.12	0.25
P_2O_5	0.05	0.05	0.04	0.04	0.06	0.04	0.09
Fe_2O_3	2.72	2.76	3.37	2.93	4.12	1.91	1.94
L.O.I.	10.17	9.60	12.32	8.38	8.92	10.48	9.49
B.S.	62	62	53	52	63	57	53

Table 1.—(Cont.)

	AG-2	*AG-8*	*AG-11*	*SP-2*	*SP-3*	*SP-4*	*SP-5*
SiO_2	80.78	85.76	84.10	77.64	75.48	76.22	74.10
Al_2O_3	6.77	4.14	5.87	7.46	6.40	5.70	7.37
MnO	0.01	0.26	0.17	0.10	0.15	0.24	0.37
MgO	0.56	0.40	0.43	1.10	1.00	0.98	1.07
CaO	0.53	0.77	0.68	1.54	4.12	2.93	4.31
Na_2O	0.18	0.12	0.30	0.17	0.19	0.25	0.29
K_2O	0.63	0.54	0.65	1.49	1.11	0.92	1.40
TiO_2	0.17	0.23	0.18	0.42	0.31	0.26	0.40
P_2O_5	0.04	0.14	0.08	0.09	0.08	0.16	0.18
Fe_2O_3	5.61	2.67	2.96	3.43	3.53	5.13	4.33
L.O.I.	4.49	4.78	4.05	6.64	7.65	6.79	8.94
B.S.	64	75	69	58	59	61	55

	ZG-3	*JH-2A*	*JH-2B*	*JH-6*	*JH-9*	*JH-12*
SiO_2	75.33	61.32	77.46	76.31	69.25	64.14
Al_2O_3	6.28	4.77	7.85	8.02	5.65	5.62
MnO	0.24	0.20	0.01	0.02	0.07	0.24
MgO	0.88	0.40	1.19	1.16	1.32	1.10
CaO	3.26	15.46	1.04	1.99	6.83	10.55
Na_2O	0.19	0.15	0.43	0.41	0.30	0.14
K_2O	1.30	0.65	1.45	1.58	0.77	0.48
TiO_2	1.33	0.15	0.27	0.23	0.27	0.15
P_2O_5	0.19	0.13	0.14	0.17	0.09	0.06
Fe_2O_3	4.23	1.56	3.14	2.98	4.37	4.61
L.O.I.	7.70	14.81	6.86	6.68	10.92	12.46
B.S.	59	49	58	56	54	50

	AB-3	AB-5	AB-6	AB-7
SiO_2	79.02	79.67	83.10	85.60
Al_2O_3	5.30	5.03	4.45	4.60
MnO	0.06	0.03	0.07	0.11
MgO	0.51	1.03	0.86	0.40
CaO	3.49	0.88	0.50	0.86
Na_2O	0.14	0.18	0.22	0.09
K_2O	0.84	0.51	0.46	0.70
TiO_2	0.30	0.28	0.30	0.26
P_2O_5	0.08	0.11	0.10	0.03
Fe_2O_3	2.80	4.19	4.04	1.98
L.O.I.	6.92	7.83	5.63	4.90
B.S.	65	67	72	74

L.O.I. = loss of ignition at 900°C.
B.S. = biogenic silica.

Most of the silica comes from the tests of radiolarians, although silica from clays and terrigenous quartz may also be present. Considering that the percentage of terrigenous quartz is very small and the mineralogy of the clays is basically smectite and illite, a first approximation to the valoration of biogenic silica can be obtained through the following formula:

$$Si_{bio} = Si_{tot} - 2.56 \times AL_2O_3$$

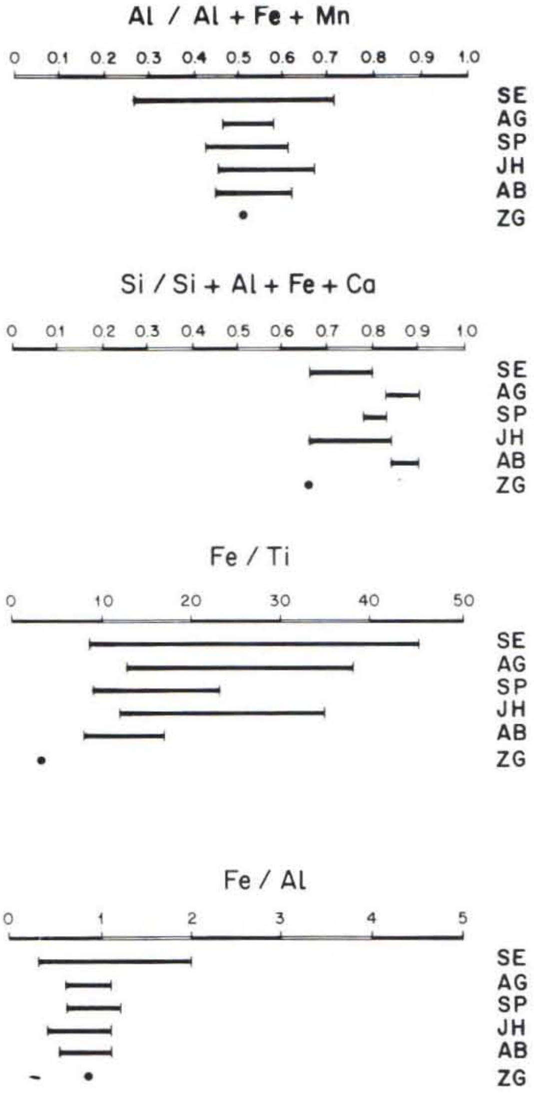

Figure 3.—Comparison of different index values of the radiolarites in the various sections.

In this formula it has been considered that the proportion of smectite and illite in the radiolarite is the same. This data agrees to a large extent with the SiO_2/Al_2O_3 relationships obtained in pelagic clays (2.5 for Weaver and Pollard 1973 and 2.26 for Brewster 1983).

Biogenic silica is more interesting than total silica since biogenic silica is a parameter of easier correlation than the total silica of the sample. Total silica has the problem that it is a parameter that jointly expresses many aspects such as radiolarian rates, clay proportion, presence of siliciclastic components and their mineralogy, etc.

Applying the formula to the rocks defined as radiolarites in this study, it has been found that the biogenic silica proportion varies according to the studied section in the following way: SE between 52% and 69%, AG between 64% y 75%, ZG 59%, SP between 55% y 61%, JH between 50% y 58% and AB between 65% and 74% of biogenic silica. According to this data, radiolarites with a biogenic contribution greater than 64% are only found in AB and AG series while radiolarites with biogenic silica lesser than 61% appear in ZG, SP, and JH series.

The existence of good correlation coefficients among oxides of samples from the same section mainly indicates that the minerals are the same in the different samples of the given section and their proportion is the only thing that changes. When this fact is produced, the regression line is another "parameter" that serves to determine a section. So, the section is characterized by a regression line and those points that are represented near such a line have more probability of belonging to this section than the distant points.

In the section studied here, only the SP and JH sections present good correlation coefficients between biogenic silica and Al_2O_3 or K_2O (fig. 4). In the SP section, the regression line for these elements presents a negative slope. This fact, from a sedimentological point of view, indicates that the radiolarian and terrigenous contributions which form the rock are in an inverse proportion. These terrigenous contributions may come from the continent. In the JH section, the slope of the regression line is positive. It means that radiolarians increase while Al_2O_3 and K_2O also increase. In this case, the Al_2O_3 and K_2O contents can be due to the presence of clays formed by a weathering of the basalts.

In general, the regression line should only serve as a criterion in excluding samples, that is to say that if a sample does not fall near the regression line it can be assured that it does not belong to the section that represents this line.

CaO contents represent the calcite quantity since the amount of CaO in the clays is usually very low. CaO contents can not be used to discriminate the different sections since each of them presents a great variability in these contents. For example, the AG section is characterized by the lower contents of CaO (<0.77) but some samples of AB also present this range of values. Although the number of samples is low, a discriminate factor can be found plotting the percentage of CaO versus the percentage of biogenic silica. In the AG section a high correlation coefficient exists (-0.98). However, the samples of the AB section can not be included in the regression line defined by the previous data from AG. The problem of this type of discrimination is that the number of samples is now very low. So, a broader study is needed to define some definitive conclusions in this respect.

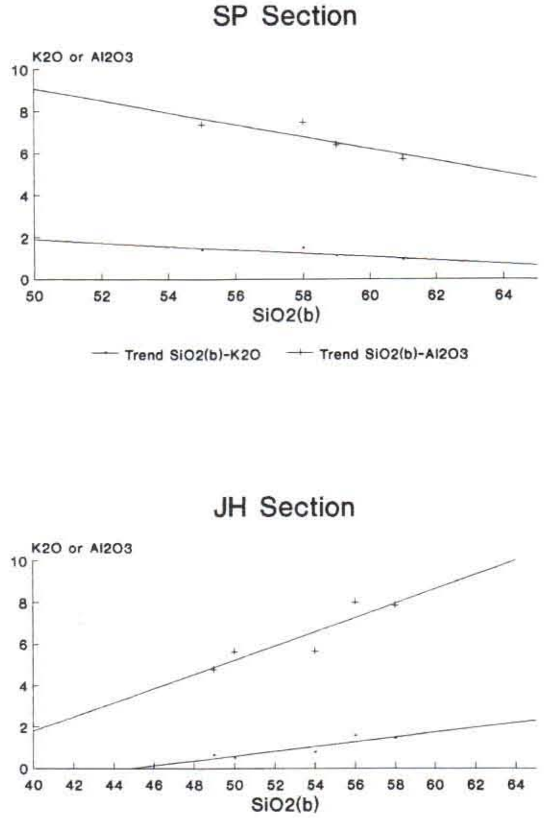

Figure 4.—Plot of biogenic silica versus K_2O and Al_2O_3 in SP and JH sections.

Finally, a statistical analysis (principal components analysis) including all the samples studied in this paper does not reveal significant results since the silica content is the variable with the greatest influence in the definition of the first principal component. Moreover, carrying out this analysis using the samples as variables, a similar influence of the different samples can be outlined to define the first principal component. So, it is not possible to dicriminate groups of samples from this PCA study.

Trace and rare earth elements

The obtained values in the trace element study do not offer positive results to discriminate groups of samples related to sections, due to the fact that all the elements generally present very similar contents, in the different series (table 2). Sometimes, some elements present variable values but in this case there is not a relationship between the variability of the element and the samples of a section.

In relation to rare earth elements (REE), cerium often behaves differently from the other REEs, due to its oxidation in some aqueous environments to relatively insoluble Ce(IV). The Ce anomaly assesses relative behavior of Ce with respect to the neighboring light REEs (LREEs) and is defined by the ratio $Ce/Ce^* = (Ce_{sample}/Ce_{shale})/Ce^*$, with Ce^* being obtained by

Table 2.—Trace and Rare Earth element composition in selected samples.

	ZG-3	*SE-3*	*SE-21*	*SE-56*	*SP-3*	*JH-9*	*JH-12*	*AG-11*	*AG-8*	*AB-6*
Ba	172	146	129	93	143	267	182	301	128	214
Be	1	<0.5	<0.5	<0.5	1	1	1	1	<0.5	1
Co	12	8	10	14	7	6	6	<5	<5	5
Cr	47	20	41	30	41	39	41	36	35	37
Cu	96	30	130	41	48	105	107	61	59	50
Ga	6	<5	5	<5	6	6	6	<5	<5	<5
Nb	6	<5	5	<5	6	6	5	<5	<5	6
Ni	36	100	60	39	31	47	6	15	20	42
Rb	65	9	35	13	43	40	35	28	24	31
Sc	11	5	8	7	10	10	8	7	7	8
Sr	58	51	77	67	62	75	75	41	38	63
Th	6	<5	6	5	5	6	<5	<5	<5	<5
V	46	25	51	33	47	50	62	38	39	50
Y	21	10	15	16	12	24	12	24	28	19
Zn	58	185	108	98	39	60	82	24	108	57
Zr	47	17	40	25	44	43	41	39	37	38
La	21	7	15	13	16	24	15	21	27	32
Nd	18	8	13	11	17	21	14	20	29	33
Eu	1	0.5	0.5	0.5	1	1	0.5	1	1.5	1.5
Dy	3	1.5	2.5	2.5	2.5	3.5	2	3.5	5	4
Yb	1.5	0.5	1	1	1	1.5	1	1.5	1.5	1.5
Ce	47	19	34	27	41	45	32	29	45	24
Sm	4	2	3	3	3.5	4.5	3	4.5	6.5	6.5
Gd	3.5	1.5	2.5	2.5	3.5	4	2.5	4	6	5
Er	2	1	1.5	1.5	1.5	2	1	2	2.5	2
Lu	0.3	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.3	0.3

linear interpolation between shale-normalized La and Pr or Nd values (Murray *et alii* 1991). Samples with Ce/Ce*<1 are considered to have a negative Ce anomaly. The character and evolution of this anomaly have been used by many authors to establish considerations about the sedimentological characterization of the deposition environment (Goldstein and Jacobsen 1988, Eldelfield 1988, De Baar *et alii* 1988, Toyoda *et alii* 1990, among others). The Eu anomaly (Eu/Eu*) is calculated in an analogous way.

Finally, variations in behavior across the REE series can be indicated by the degree of heavy REEs (HREEs) enrichment with respect to LREEs, here defined as the ratio

$$Lu_n/La_n = (Lu_{sample}/Lu_{shale})/(La_{sample}/La_{shale}).$$

These three indexes (Ce/Ce*, Eu/Eu* and Lu_n/La_n) let us know more or less the exact behavior of the rare earth elements. Inasmuch as looking for criteria to discriminate samples, these indexes can be interesting. So, Ce/Ce* index separates three group of samples with different values: the AB samples with Ce/Ce* values near 0.36, the AG samples with values ranging from 0.68 to 0.78 and the rest of the samples with values ranging from 0.94 to 1.29. In relation to the Eu/Eu* index, the results of this index are not satisfactory since all the samples are near 0.98 and 1.08. Finally, the Lu_n/La_n ratio lets us separate some samples. From all these aspects it can de deduced that the combination of the Ce/Ce* index and the Lu_n/La_n ratio can be a useful method to discriminate the different types of samples (fig. 5).

Concluding remarks

1) The studied radiolarites do not present any homogeneous petrological or geochemical characteristics along the different sections (AB, AG, etc.). Due to this, the exclusive utilization of absolute petrological and geochemical data can not characterize each section.

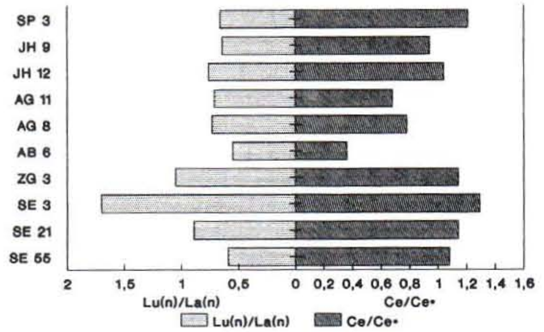

Figure 5.—Plot of the Ce/Ce* index versus Lu_n/La_n index in some radiolarites from different samples.

2) Chemical composition is preferable to mineralogical composition as a general characterization criterion. The radiolarites possess a small proportion of non-silica minerals, and that is why their quantification is difficult. Due to that the study of the chemical composition offers more differentiating criteria than the study of mineralogical composition. However, both methods must be jointly used in order to achieve a correct interpretation.

3) The analysis of major, minor, trace and rare earth elements is the best method to separate radiolarites among the studied sections. According to this, biogenic and total silica let us define two groups of sections: (a) AB and AG, and (b) ZG, SP and JH, while the SE section is not clearly defined. In the first group, AG and AB sections differentiate themselves when the percentage of biogenic silica (greater than 64%) is compared to the percentage of CaO. The AG samples adapt themselves to a typical regression line, and the AB samples are distant from the regression line. Furthermore the samples of the AB section clearly characterize themselves by Ce/Ce* and Lu_n/La_n indexes. In relation to the second group (<61% of biogenic silica), the samples from the SP and JH sections are defined by a typical regression line when the percentage of biogenic silica is compared to the percentage of Al_2O_3 or K_2O. The SE section remains undefined.

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