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Sea Water Basalt Interaction in Spilites From the Iberian Pyrite Belt

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Abstract. Low grade hydrothermally metamorphosed mafic rocks from the Iberian Pyrite Belt are enriched in ^{18}O relative to the oxygen isotopic ratio of fresh basalt ($+6.5 \pm 1\,^0/_{00}$). The observed δ^{18}O whole rock values range from $+10.87\,^0/_{00}$ to $+15.71\,^0/_{00}$ corresponding to positive isotopic shifts of $+5\,^0/_{00}$ to $+10\,^0/_{00}$, thus requiring isotopic exchange with fluids under conditions of high water:rock ratios at low temperatures. The lowest δ^{18}O observed corresponds to an albitized dolerite still and is compatible with independent geochemical data suggesting lower water: rock ratios for the alteration of these rocks.

The isotope data are consistent with the hypothesis that the spilites from the Pyrite Belt were produced by interaction of basaltic material with sea water.

Significant leaching of transition metals from the mafic rocks during alteration coupled with available sulphur isotopic data for the sulphide ores also suggest that sea water may have played an important role in the formation of ore deposits in the Iberian Pyrite Belt.

1. Introduction: Background Information Concerning the Origin of Spilites in the Iberian Pyrite Belt

Spilitised volcanic flows and albite-doleritic sills are widespread in the Iberian Pyrite Belt (Kleyn 1960; Carvalhosa 1961; Cruz Gaspar 1961; Rambaud Perez 1969; Strauss 1970; Schermerhorn 1970). They correspond to the mafic member of a bimodal magmatic suite which represents the igneous stage in the development of the Pyrite Belt geosyncline which occurred from late Devonian to lower Visean times (Schermerhorn 1971; Carvalho 1976). The occurrence of radiolarian chert filling the interstices in pillow lavas (Williams 1966) indicate that the volcanism took place in a submarine environment.

Both the volcanic and enclosing sedimentary rocks were deformed during the Hercynian orogeny. Low-grade regional metamorphism was contemporaneous with, and to some extent postdated the main (first) folding phase (Schermerhorn 1975a; Munhá 1976). However, primary volcanic structures are still preserved in less deformed rocks, and this, combined with textural and mineralogical evidence clearly indicate that the mafic rocks acquired their spilitic character prior to the onset of the regional metamorphic episode.

The various proposals concerning the origin of spilites in the Pyrite Belt may be summarized as follows:

(1) spilites are derived by primary magmatic crystallization. The initial melt may have been either a spilitic magma (Rambaud Perez 1969; Schermerhorn 1975b) or, basaltic modified by contamination prior to extrusion (Soler 1973);

(2) spilites are the result of sub-solidus hydrothermal alteration of basaltic rocks (Munhá 1979).

Considering the high degree of variance of the major element oxide analyses for spilites (Fig. 1), in

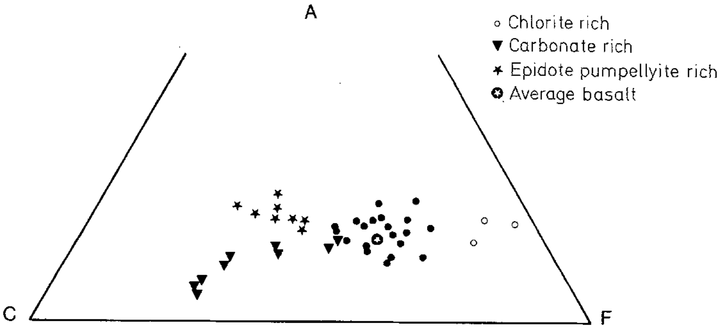

Fig. 1. ACF diagram showing the chemical variation of the Iberian Pyrite Belt spilitic rocks. $A = Al_2O_3 - Na_2O - K_2O$; $C = CaO$; $F = FeO + MnO$

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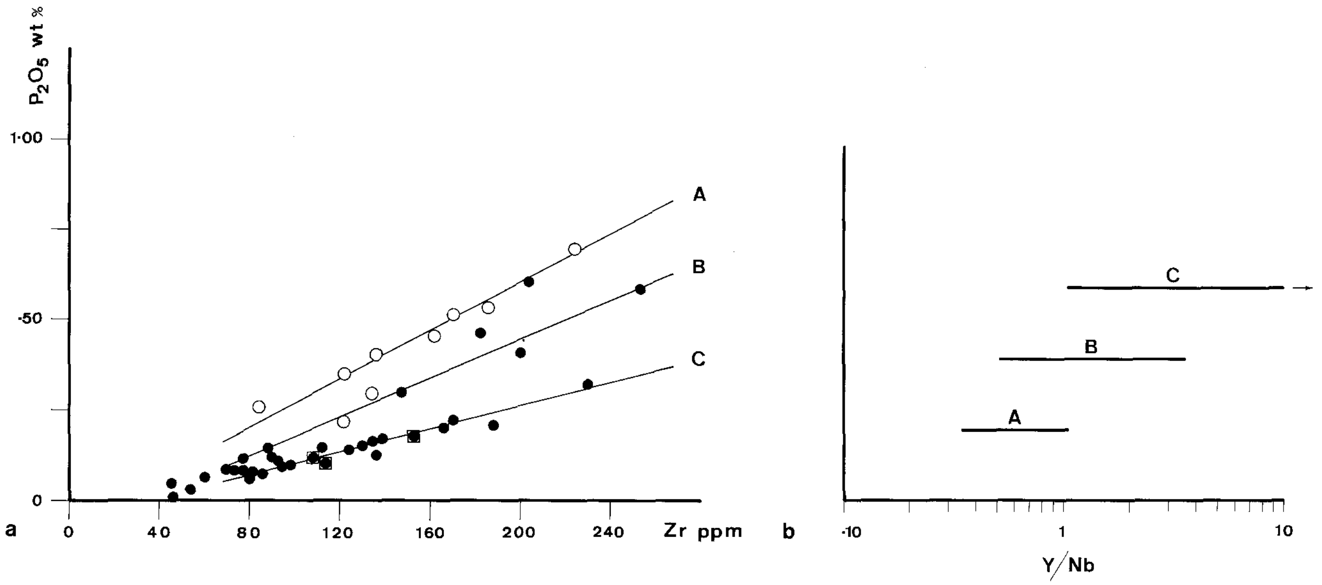


Fig. 2a and b. Distribution on the P_2O_5-Zr diagram (**a**), and Y/Nb ratios (**b**) for the Iberian Pyrite Belt spilitic rocks; *squares:* lower lavas; *open circles:* upper lavas; *filled circles:* doleritic sills (after Munhá 1979)

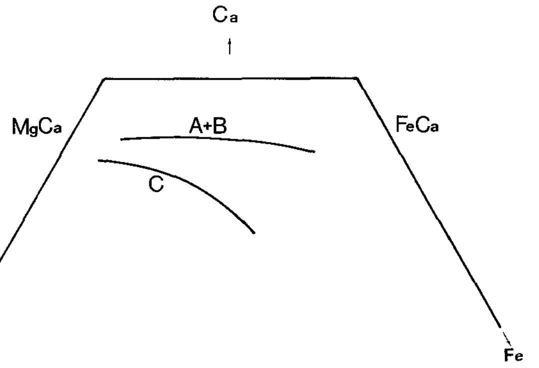


Fig. 3. Schematic compositional trends of clinopyroxenes occurring as relict phases in the Iberian Pyrite Belt spilitic rocks (Munhá, unpubl. data). **A**, **B**, and **C** represent the same sample groups as in Fig. 2

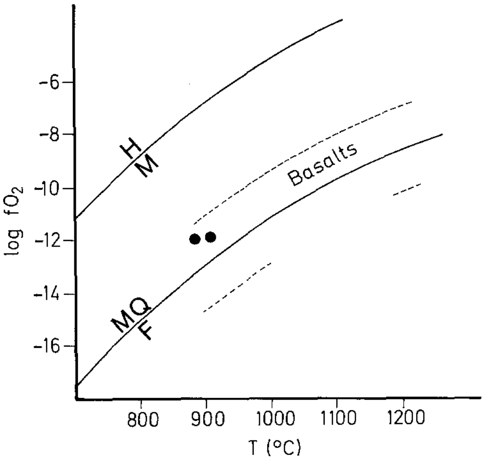


Fig. 4. Equilibration temperature and fO_2 of (relict) coexisting iron-titanium oxides in dolerites (2 samples), (Fe-Ti oxides coexist with biotite + amphibole in both samples; Munhá, unpubl. data). Basalts filed is slight modified after Carmichael et al. (1974)

combination with the systematic covariance of the relatively "immobile" elements (Pearce and Cann 1973; and Fig. 2), and the congruent relationship between these and the chemical characteristics of relict high temperature phases (Fig. 3), make both variants of model 1 very unlikely. The occurrence of calcic-plagioclase plus Mg-olivine, coupled with geothermometric data from coexisting Fe-Ti oxides all indicate minimum temperatures in the order of 900° C (Fig. 4) providing further support for the above conclusion, and suggest in addition that the spilitic rocks must have been derived from basalts due to mineral transformations which took place under sub-solidus conditions.

The objective of this work is to describe and interpret various aspects of oxygen isotope geochemistry of spilitic rocks from the Iberian Pyrite Belt. The hypothesis of spilite generation in the Pyrite Belt as a consequence of hydrothermal activity related to sea water circulation (Munhá 1979) is further examined in the light of the new geochemical data, and some speculative views are presented concerning the implications of the general process on massive sulphide ore formation.

2. Hydrothermal Metamorphism

Because the Pyrite Belt mafic rocks have been metamorphosed to mineral facies in which albite is stable, it is not easy to define the spilitic mineral composition prior to regional metamorphism. However, a drastic decrease in porosity and/or permeability caused by the earlier generation of new hydrothermal minerals must have created highly unfavourable conditions for attaining re-equilibration (see Aguirre et al. 1978). Consequently, the low grade regional metamorphic episode, which took place later would not have significantly affected the preexisting hydrothermal mineral assemblages. For this reason, the study of the least deformed rocks, from the lower regional metamorphic grades, usually provide information on the earlier spilitization process.

The extent of the spilitization reactions appears to have been markedely heterogeneous, and primarly conditioned by the initial anisotropy in permeability of the basaltic material. An almost complete mineralogical readjustment took place in the highly vesicular and venulated lavas whereas the more impermeable sills exhibit a lower degree of alteration except at their marginal zones. This observation provides the best evidence that these rocks have been in contact with an external circulating fluid; i.e. affected by hydrothermal alteration, the variable intensity of which was essentially a function of differing water: rock ratios and permeability.

The hydrothermal metamorphic grade ranges from zeolite facies mineral assemblages characterized by the (rare) occurrence of zeolites and clay minerals, through chlorite-epidote bearing assemblages, to low grade greenschist facies characterized by chlorite-actinolite-epidote. Also, in some gabbroic cumulate rocks, the hydrothermal alteration produced mineral assemblages characterized by grossular-tremolite-diopside. By comparison with parageneses developed in geothermal systems (Keith et al. 1968; Kristmannsdottir and Tomasson 1978), combined with available experimental data (Liou 1971), it is suggested that the hydrothermal metamorphism of the mafic rocks in the Pyrite Belt took place under temperatures ranging from 50°–100° C to 350°–400° C.

It is worth noting the following mineralogical changes with increasing metamorphic grade (see Table 1):

(1) increase in abundance of Ca-rich aluminosilicates;

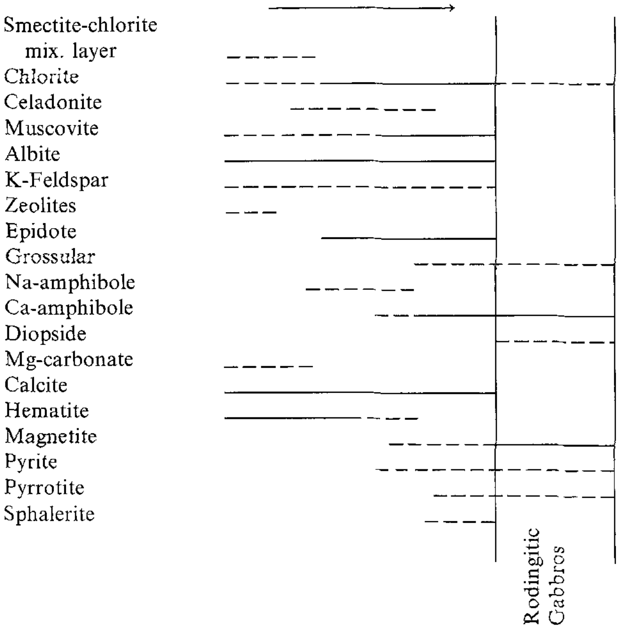
(2) decrease in Mg/Ca ratio in carbonates;

(3) progressive replacement of hematite by magnetite+sulphides, and of riebeckite by actinolite.

These mineralogical changes seem to indicate that the fluid responsible for the hydrothermal alteration, originally oxygenated and Na-rich, became progressively reduced and Ca-enriched (and probably somewhat Mg-depleted) as it reacted at progressively higher temperatures with the basaltic rocks.

The inferred geochemical trend is similar to that observed both in sea water derived geothermal brines (Tomasson and Kristmannsdottir 1972), and in solutions resulting from experimental basalt-sea water interaction systems (Bischoff and Dickson 1975; Hajash 1975; Motll and Holland 1978). Further evidence for large-scale sea water spilitisation reactions is provided by the rodingitic gabbro occurring near the Tharsis mine (Huelva), which is similar to rodingite formed by rapid hydrothermal discharge through basalts at modern mid-ocean ridges (Honnorez and Kirst 1975).

Table 1. Increasing metamorphic grade



In summary, the mafic volcanic rocks from the Iberian Pyrite Belt represent products of submarine volcanism, and it has been shown that they underwent hydrothermal alteration prior to the onset of tectonic deformation and regional metamorphism (Munhá 1979). The development of the secondary spilitic mineral assemblages described above, which involved extensive hydration, carbonatization and oxidation, clearly required introduction of CO_2-rich and oxygenated fluid from some readily available external reservoir. From the evidence presented it is concluded that the spilites developed in a sub-sea floor geothermal system involving circulation of brine, which underwent chemical and thermal evolution while interacting with the various rock types, prior to discharge onto the sea floor.

3. Oxygen Isotope Geochemistry

(a) Sampling and Analytical Methods

The material selected for oxygen isotope analyses consists of seven whole rock samples, one albite mineral separate, and a quartz-chlorite mineral pair from a hydrothermal vein. The analysed mafic rocks (5) are thought to represent low to medium grades within the previously described hydrothermal metamorphic range. The

Table 2. $\delta^{18}O$ of whole rock and mineral samples from the Iberian Pyrite Belt

Sample n°.	Whole rocks	$\delta^{18}O$	Fe_2O_3/FeO^t	L.O.I.
540-P. 12	meta-dolerite	+10.87	0.39	4.21
547-P. 34	spilite	+13.97	0.75	10.65
555-P. 3	spilite	+12.00	0.58	8.48
559-P. 102	spilite – pillow lava	+13.42	0.72	6.61
2806 SD	spilite – pillow lava	+15.71	0.76	8.38
567-P. 61	albitophyre	+13.09	0.64	8.85
544-P. 25	rhyolite	+12.11		
	Minerals			
559-P. 102	albite	+13.82		
1907 SD	quartz recharge vein	+19.89		
1907 SD	chlorite	+5.58		

remaining two samples correspond to an albytophire and to an oxydized rhyolite respectively (see Table 2).

Conventional techniques were employed for the extraction of oxygen from minerals with bromine pentafluoride and quantitative conversion to carbon dioxide, prior to mass spectrometric analyses (Clayton and Mayeda 1963). Isotopic data are reported as $\delta^{18}O$ values in permil relative to standard mean ocean water (SMOW).

(b) Oxygen Isotope Data and Interpretation

Oxygen isotope geochemistry has been shown to be an useful technique for geothermometry (Javoy 1977), for suggesting possible sources of fluids that have exchanged with rocks (Taylor 1974; Sheppard 1977), and for the clarification of certain aspects of mass transfer (Spooner et al. 1977; Norton and Taylor 1979). It is particularly applicable to the study of altered mafic rocks because their initial isotope ratios are relatively uniform (+6.5±1‰, Taylor 1979), and thus provide a reference against which to compare the alteration products. During the passage of fluid through rocks the concentrations of many elements are controlled by the solubility and ion exchange equilibria between the fluid and its wallrocks. The stable isotope ratios of oxygen vary in different rocks, minerals and natural terrestrial fluid reservoirs, and are also involved in fluid-rock isotope exchange reactions. As a result, during water/rock interaction, the oxygen isotope ratios of rock and/or fluid may be shifted away from their initial values.

The $\delta^{18}O$ values for the analysed volcanic rocks and minerals are presented in Table 2, and compared with other oxygen isotope data in Fig. 5.

All the mafic rocks are enriched in ^{18}O relative to a $\delta^{18}O$-value +6.5±1‰ which characterises unmodified basaltic material. The observed $\delta^{18}O$ whole rock values range from +10.87‰ to +15.71‰, corresponding to positive isotopic shifts of +5‰ to +10‰. These enrichments in ^{18}O are similar to the enrichments observed in low grade sub-seafloor hydrothermally metamorphosed basaltic rocks (Muehlenbachs and Clayton 1972; Spooner et al. 1974; Heaton and Sheppard 1977); but contrast with the ^{18}O depletions observed in basalts that have undergone high-temperature (>400° C) marine hydrothermal alteration (Fig. 5), or in continental basalts which have been hydrothermally altered by interaction with isotopically light meteoric waters (Forester and Taylor 1976). In fact, as already mentioned, the mafic volcanic rocks studied here represent the products of submarine volcanism which have been converted to spilites due to hot water-rock interaction related to sub-seafloor hydrothermal activity. Such

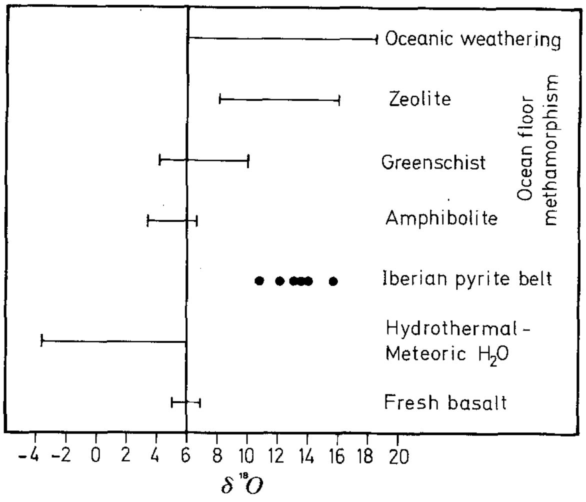


Fig. 5. Whole rock oxygen isotope ratios of hydrothermally metamorphosed igneous rocks from the Iberian Pyrite Belt. Comparative data from: Spooner et al. (1974, Fig. 1) and Heaton and Sheppard (1977, Fig. 4)

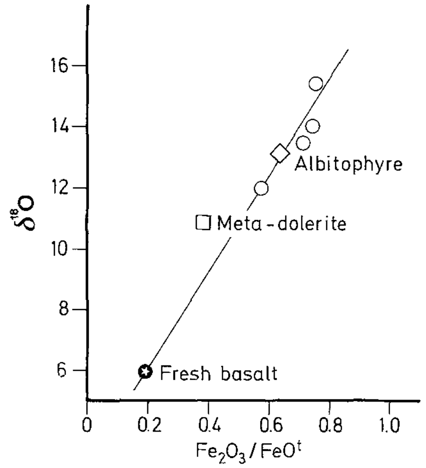


Fig. 6. Whole rock oxygen isotope ratios plotted against oxidation ratios of spilitic rocks from the Iberian Pyrite Belt

a process could not have involved significant amounts of meteoric waters. The results presented by Munhá (1979) coupled with the oxygen isotope data discussed above also make it unlikely that juvenile (magmatic) water was important. In particular, the fact that hydrothermal alteration opperated over large areas producing, in some cases, highly oxidized assemblages (Fig. 6), suggest that modified sea water was the principal component of the hydrothermal fluid (Spooner and Fyfe 1973).

Isotopic temperatures in the range 100°–140° C were calculated from coexisting quartz and chlorite in a hydrothermal recharge vein, which cuts through highly oxidized pillow lavas near São Domingos Mine. Quartz-chlorite fractionations have been interpreted with respect to the quartz-water and chlorite-water equations given by Clayton et al. (1972), Mathews and Beckinsale (1979), and Wenner and Taylor (1971). Assuming temperatures of 100° to 140° C, the calculated $\delta^{18}O$ of water in equilibrium with the vein quartz is $0^0/_{00} \pm 1^0/_{00}$. This is in close correspondence with the $\delta^{18}O$-value of present day sea water, which has probably remained at about $0^0/_{00}$ throughout most of geological history (see Knauth and Lowe 1978). While this isotopic temperature is approximate the result is consistent with what should be expected from the observed metamorphic assemblages. The metamorphic temperature range for the analysed mafic rocks is considered to have been from 50° C to 350° C, from mineralogical criteria. Examination of available silicate-water fractionation data (see Taylor 1979) clearly shows that for this temperature range rock-water isotope fractionations must be large and positive. Therefore, at these low temperatures, basaltic material affected by sea water interaction may become enriched in ^{18}O. Differences in the observed $\delta^{18}O$-values are easily explained in terms of different secondary modal composition of the analysed rocks, which reflects variable temperature, and/or water/rock ratios during hydrothermal alteration (see Spooner et al. 1974). For example, the lowest determined $\delta^{18}O$ corresponds to a relatively impervious massive doleritic sill (540–P. 12), which also shows the lowest Fe_2O_3/FeO^t and L.O.I. values, thus suggesting that it interacted with a smaller amount of fluid. Also, the insipient development of actinolite needles overgrowing relict clinopyroxene seems to indicate higher temperatures during the alteration of this rock. In general, however, the magnitude of the observed isotopic shifts requires isotopic exchange with fluids under conditions of high water/rock ratios and at low temperatures (compare with Spooner et al. 1977).

The correspondence between the isotopic shifts predicted and those observed, as well as the calculated isotopic composition of the hydrothermal fluid ($0^0/_{00} \pm 1^0/_{00}$), strongly corroborates the hypothesis that the spilites from the Pyrite belt were produced by interaction of basaltic material with sea water.

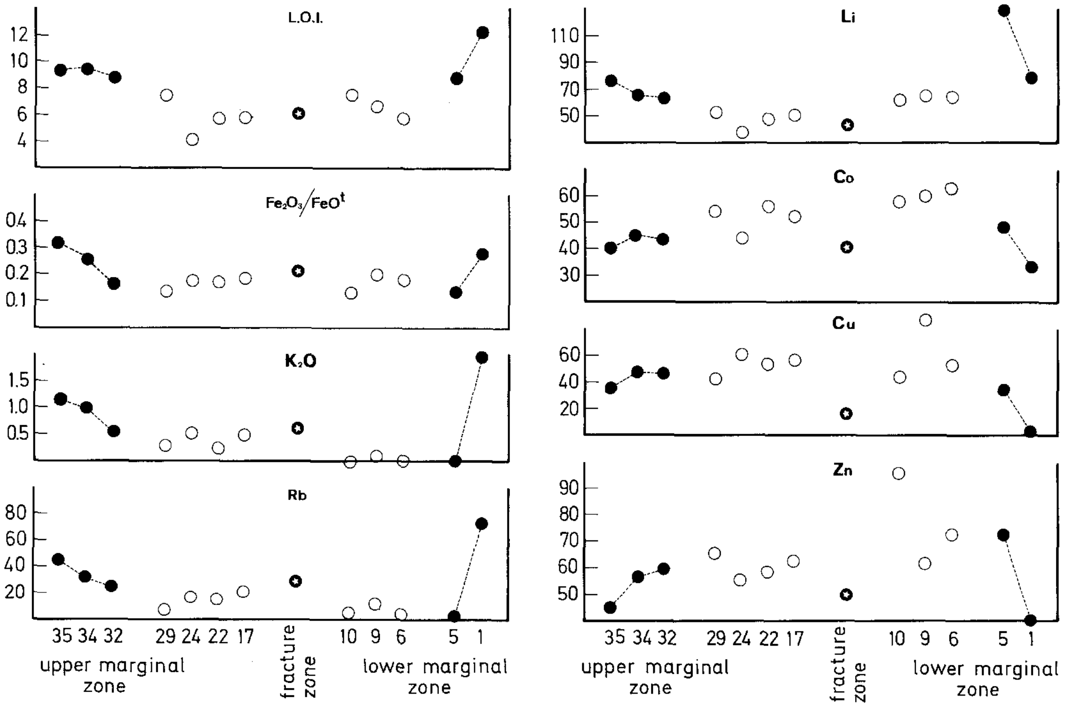


Fig. 7. Selected major and trace element variations in the doleritic sill intercepted by drilling at Garrochal

Table 3A. Chemical analysis of meta-volcanic rocks from the Iberian Pyrite Belt

Sample n°[a]		540-P. 12	547-P. 34	555-P. 3	559-P. 102	2806 SD	567-P. 61	544-P. 25
SiO_2	wt.%	50.21	43.42	43.81	48.81	44.40	49.36	75.57
TiO_2		2.14	2.39	1.87	1.33	1.92	0.64	0.09
Al_2O_3		14.28	13.69	15.36	17.50	17.84	16.66	10.53
Fe_2O_3		4.40	6.87	4.20	6.68	10.22	3.19	3.42
FeO		7.26	3.03	3.49	3.38	4.32	2.12	0.12
MgO		5.28	3.93	5.50	3.10	0.92	2.45	nd
CaO		7.38	10.98	9.44	7.56	6.36	9.49	nd
Na_2O		3.53	1.86	3.49	5.13	4.42	6.77	0.43
K_2O		0.05	2.72	3.23	0.01	0.81	0.05	8.73
P_2O_5		0.18	0.43	0.19	0.08	–	0.08	nd
MnO		0.28	0.10	0.19	0.31	0.30	0.24	0.01
L.O.I.		4.24	10.65	8.48	6.61	8.38	8.85	0.73
Total		99.20	100.07	99.25	100.50	99.89	99.90	99.63
Li	ppm	18	44	52	41	38	19	7
Rb		2	67	37	3	51	5	225
Sr		327	272	267	176	235	184	12
Ba		123	171	731	50	389	39	426
Sc		43	22	22	40	54	–	–
Y		45	20	28	17	42	13	91
Zr		188	149	122	59	81	113	385
Nb		10	38	39	5	8	5	40
Cr		134	201	235	247	53	137	1
Co		47	33	34	40	43	–	–
Ni		20	137	121	66	14	85	nd
Cu		56	27	25	9	16	13	16
Zn		64	27	75	55	–	32	52
La		24.5	54.9	41.7	8.9	11.1	–	10.4
Ce		49.3	81.8	67.1	21.5	21.9	–	20.1
Pr		7.2	9.2	9.2	2.9	3.6	–	3.0
Nd		32.9	35.8	37.7	13.7	17.1	–	13.4
Sm		8.4	6.8	7.5	3.6	4.9	–	5.6
Eu		2.3	1.8	1.9	1.2	2.0	–	0.4
Gd		9.1	5.9	7.4	3.9	5.9	–	9.4
Tb		1.7	0.9	1.0	0.6	1.1	–	2.4
Yb		5.2	1.6	2.2	1.0	4.0	–	10.0

[a] Sample n° are the same as in Table 2

4. Chemical Changes During Basalt-Sea Water Interaction

As shown in Fig. 1 the hydrothermal metamorphism which affected the Iberian Pyrite Belt mafic rocks was strongly non isochemical, and involved the mobilization of several major elements.

To obtain information on the chemical effects of hydrothermal alteration, several samples, exhibiting different degrees of alteration, were analysed from a meta-doloritic sill intercepted by drilling near Garrochal (South Portugal). The analytical results show (see Fig. 7 and Table 3B) that with increasing intensity of alteration (as indicated by increasing amounts of volatiles and higher Fe_2O_3/FeO^t ratios) the basaltic rock becomes enriched in alkaline elements (K, Rb, Li), and exhibit a concomitant leaching of transition metals (Cu, Co, Zn). The following reactions represent schematically these chemical changes and also account for the observed variations in the modal composition of the studied samples:

(a) Oxidation

$11\ Fe_2SiO_4 + 2\ SO_4^{2-} + 4\ H^+$
$= 7\ Fe_3O_4 + FeS_2 + SiO_2 + H_2O$ (Spooner and Fyfe, 1973).

(b) Fixation of Alkaline Metals

$CaAl_2Si_2O_8 + CO_2 + H_2O$
$= CaCO_3 + Al_2Si_2O_5(OH)_4$.

$3\ Al_2Si_2O_5(OH)_4 + K_2CO_3$ (sol)
$= 2\ KAl_2(AlSi_3O_{10})(OH)_2 + CO_2 + 4\ H_2O$
(Fyfe 1974).

Table 3B. Chemical analysis of the doleritic sill intercepted by drilling at Garrochal

Sample n°[a]		GA6-1	GA6-5	GA6-6	GA6-9	GA6-10	GA6-17	GA-22	GA6-24	GA6-29	GA6-32	GA-34	GA6-35
SiO_2	wt.%	43.96	48.01	47.11	46.94	46.61	48.09	48.41	49.35	47.93	48.69	45.13	45.04
TiO_2		2.12	2.21	1.98	2.07	2.14	1.79	1.99	1.86	2.42	2.39	2.46	2.49
Al_2O_3		14.07	14.95	14.29	14.77	14.68	15.58	15.08	14.22	14.25	13.10	14.73	14.84
Fe_2O_3		2.87	1.87	1.98	2.30	1.54	1.81	1.90	1.69	1.60	1.63	3.01	3.51
FeO		7.53	11.36	8.94	9.17	10.01	7.95	8.99	7.83	9.87	10.22	9.02	8.24
MgO		4.43	9.59	8.51	8.97	8.02	7.99	7.90	8.10	9.85	9.68	9.66	9.87
CaO		10.49	1.35	9.23	6.82	6.93	7.87	7.83	9.55	3.73	4.79	4.76	5.07
Na_2O		nd	1.51	1.87	1.90	1.95	1.51	2.75	2.34	2.14	0.17	0.30	0.53
K_2O		1.97	nd	0.01	0.11	nd	0.51	0.25	0.56	0.31	0.59	1.07	1.15
P_2O_5		0.17	0.16	0.16	0.14	0.13	0.12	0.14	0.13	0.19	0.21	0.20	0.19
MnO		0.28	0.22	0.23	0.22	0.21	0.25	0.24	0.25	0.20	0.17	0.17	0.18
L.O.I.		12.05	8.60	5.65	6.35	6.57	5.73	5.43	4.12	7.22	8.64	9.30	9.27
Total		99.94	99.83	99.93	99.59	98.79	99.20	100.91	100.00	99.71	100.27	99.81	100.38
Li	ppm	78	128	65	67	63	51	48	38	53	63	65	76
Rb		72	3	4	12	5	21	15	17	7	24	32	45
Sr		108	70	103	142	–	177	170	179	83	40	83	60
Ba		217	nd	35	66	–	211	77	184	75	61	118	104
Sc		42	53	35	38	–	32	38	47	53	54	53	–
Y		41	43	41	43	–	35	42	39	45	45	50	47
Zr		144	154	140	139	–	125	145	132	170	159	160	170
Nb		2	5	3	3	–	2	3	2	7	5	4	6
Cr		229	263	264	259	–	254	231	–	240	222	258	258
Co		34	55	63	60	58	52	56	44	54	43	45	40
Ni		50	55	122	110	–	90	50	–	25	35	36	36
Cu		2	34	53	86	44	56	53	60,	42	45	47	35
Zn		40	73	73	62	96	63	59	56	66	60	57	45

[a] See Fig. 7 for sample localization

(c) Leaching of Transition Metals

$MO\ (solid)+2\ HCl\ (sol)=MCl_2\ (sol)+H_2O$
(see Crerar and Barnes 1976).

Thus, as result of deep penetration into heated volcanic rocks sea water changes from an oxidizing slightly alkaline solution to a reducing slightly acidic solution characterized by high concentrations of dissolved transition metals (Bjornsson et al. 1972; Seyfried and Bischoff 1977). Transition metals are leached from the volcanic rocks and transported, probably as metal halides toward the venting area of the hydrothermal system. Here the reduced brine reacts with cold, unmodified sea water with consequent precipitation of highly insoluble iron and base metal sulphides (see Helgeson 1970).

5. $^{34}S/^{32}S$ Isotope Ratios in the Pyrite Belt Sulphides

Extremely large pyrite massive sulphides are located in the Iberian Pyrite Belt. Their geology have been reviewed extensively by Rambaud Perez (1969). Strauss (1970), Garcia Palomero (1977), Routhier et al. (1977), and Strauss et al. (1977), and there is now an unanimous acceptane of a syngenetic, synsedimentary origin for the massive sulphide ores (Kinkel 1962; Schermerhorn 1971b; Bernard and Soler 1974). The massive ores are often underlained by stockwork ores which are interpreted as the hydrothermal feeder channels of the sedimentary sulphides (Williams et al. 1975; Garcia Palomero 1977).

Sulphur isotope compositions for pyrite in the Pyrite Belt orebodies have been reported by a number of workers (Rambaud Perez 1969; Williams et al. 1975; Routhier et al. 1977). The results are summarized here in order to establish some constraints on the source of sulphur. The $^{34}S/^{32}S$ ratios have been analysed in pyrites from stockwork disseminations (average $+8.5^0/_{00}$), veins ($+4.3^0/_{00}$; 1 sample), massive sulphide ores (lower central zone average $+3^0/_{00}$; border zone average $+2^0/_{00}$), and from disseminations in chert (average $-24^0/_{00}$) that overlies some of the massive sulphide deposits. Although there are variations among different deposits, at a single mine the sulphur isotopic compositions of pyrite from each of the different paragenetic types tend to be similar. The main source of sulphur has been interpreted as magmatic (Rambaud Perez 1969; Williams et al. 1975).

Unlike oxygen isotopes, however, sulphur isotopes fractionate not only among sulphur bearing solid phases but also among several possible oxidized and reduced sulphur species in solution. Therefore, the $\delta^{34}S$ value of a given hydrothermal sulphide mineral is controlled by the f_{O_2} and pH values of the solution as well as by the temperature and isotopic composition of the hydrothermal fluids (Ohmoto 1972, 1979). Knowledge of these parameters is thus required before any unique interpretation can be made on the isotopic composition of sulphide minerals.

On the basis of the hydrothermal mineral assemblages (quartz-chlorite-sericite-epidote-calcite) the temperatures for stockwork mineralization may be estimated at 250°–350° C. Extensive chlorite alteration, as well as the occurrence of sericite ± K-feldspar assemblages associated with the stockwork sulphides suggest, by analogy with modern geothermal systems (Ellis 1979) and experimental work (Hemley 1959), pH values near neutrality or slightly acidic at the temperatures quoted above. In the system Fe-Cu-S-O, pyrite and calcopyrite are the most abundant minerals whereas magnetite is rare and pyrrhotite is virtualy absent in every case. Barite occurs sporadically both in the stockwork and massive ores (Garcia Palomero 1977). Thus, the probable pH-f_{O_2} region of the sulphide ore deposition can be defined approximately by the magnetite-pyrite stability boundary, the barite solubility boundary and the stability of K-mica (see Ohmoto 1972).

If the $\delta^{34}S$ value of total sulphur in the hydrothermal fluid were around $0^0/_{00}$ (i.e. sulphur of magmatic origin) then the $\delta^{34}S$ of pyrite should have been largely negative, down to $-21^0/_{00}$ at 250° C and in the probable pH-f_{O_2} region of ore deposition. Since Devono-Carboniferous sea water, with a $\delta^{34}S$ value of $+16^0/_{00}$ for dissolved sulphate (Hoefs 1973), was the only readily accessible source of high $\delta^{34}S$ sulphur, the observed isotopic data can best be explained by considering reduced sea water sulphate as the main source of sulphur in the pyritic ores.

The decrease in the pyrite $\delta^{34}S$ values towards the top of the massive ores reflects an increase in the SO_4^{2-}/H_2S in the fluid (see Ohmoto 1979), indicating lower temperature and/or higher f_{O_2} and pH conditions during the final stages of massive sulphide deposition. The narrow range for stockwork pyrite $\delta^{34}S$ values would also require that the SO_4^{2-}/H_2S ratio remained relatively uniform during stockwork mineralization; this is the result of the large buffering capacity of fluids in hydrothermal systems which evolved under conditions of high water/rock ratios.

6. Discussion

Mineralogical and geochemical data presented above clearly indicates that the spilitic rocks from the Iberian Pyrite Belt were produced by sub-solidus alteration of basaltic and doleritic rocks. During the alteration process metamorphic assemblages characteristic of the zeolite and greenschist facies developed and singificant redistribution of several major and trace elements took place. Increase in water contents, strong carbonatization and considerable changes in iron oxidation ratios (see Munhá 1979), reflecting the development of secondary minerals, all indicate that the metamorphism was the consequence of water-rock interaction at elevated temperatures. The oxygen and sulphur isotopic data strongly implies that sea water was not only the fluid which hydrothermally metamorphosed the mafic rocks but also played an important role in the precipitation of the sulphide ores.

The observed $^{18}O/^{16}O$ and $^{34}S/^{32}S$ isotopic ratios indicate that the alteration process must have taken place under conditions of high water/rock ratios thus suggesting that the hydrothermal system involved vigorous circulation of fluids. Fluid motion might have been related with thermally driven convective circulation as a result of heat released due to widespread, contemporaneous igneous activity in the area (Lister 1972; Wolery and Sleep 1976; Norton and Knight 1977; Norton and Cathles 1979). Whether or not convective flow in a porous medium is possible depends on the thermal gradient. The vigour of flow is described by an appropriate Rayleigh number and for vigorous flow, gradients in excess of the adiabatic gradient and high permeabilities are required. A conservative estimation of a Rayleigh number for the conditions of hydrothermal activity in the Pyrite Belt, (permeability = 15 md; $\Delta T = 400°$ C; $\Delta H = 500$ m = thickness of the Volcano-sedimentary Complex) yields values (4×10^2) which clearly exceed the critical Rayleigh number for which convection occurs (18–27 for an open top and uniform lower boundary condition, Lapwood 1948), thus suggesting that not only convective circulation of fluids was possible but also that it must have proceeded in a vigorous manner.

By analogy with active geothermal systems downward migration of sea water into the volcanic rocks occurred over a large area, and upward discharge was localized. The influx of sea water deep into the volcanic pile must have been related to thermal contraction fracturing and increasing permeability as described by Lister (1974). The massive sulphide deposits are interpreted to have formed in localized basins at the volcanic rock-sea water interface, their underlying stockwork zones representing the focused hydrothermal discharge zones which most probably were tectonically controlled by pre-existing fault and/or fracture systems (Oliveira 1971; Carvalho 1977).

During sea water-volcanic rock interaction halide concentration tends to rise (Ellis and Mahon 1964, 1967), and the brine becomes increasingly saline and progressively reduced by reaction with the iron bearing silicate minerals of the rocks. Its sulphate content is reduced to produce disseminated sulphides and magnetite and salinity may increase as a result of extensive formation of highly hydrated minerals which characterize spilites. Several experimental studies and direct observation of active geothermal systems have shown that this chemically modified sea water is able to leach significant amounts of metals from rocks, which are then transported mainly as soluble metal chloride complexes. When this reduced, metal rich brine is discharged into sea floor, and as it mixes with sea water, sulphate from sea water is reduced near the vent providing the sulphur which combines with iron and base metals causing their precipitation as metal sulphides.

The general hydrothermal model summarized above has already been successfully applied to explain the formation of massive sulphide ore bodies such as Cyprus (Spooner 1977) and Kuroko (Ohmoto and Rye 1974), and extant metal rich deposits observed at ocean ridge crests (Edmond et al. 1979), as well as the generation of spilitic rocks often associated with them (see Andrews and Fyfe 1975). The data presented here strongly suggests that the hypothesis of hydrothermal activity, related to thermally driven convection of sea water, is also applicable to explain the general features of spilitization and massive sulphide ore formation in the Iberian Pyrite Belt.

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