Aluminium mobility in hydrothermally altered granites

Mobilidad del aluminio en granitos hidrotermalmente alterados

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ABSTRACT

Immobile elements are used to evaluate metasomatism caused by hydrothermal alteration in Linares granite related to Ba-(base metals) veins. Mass transfers of Aluminium (which is commonly considered as the best monitor) are been detected by correlating the monitor elements, being Zr used as more reliable monitor.

RESUMEN

El metasomatismo de la adamellita de Linares, causado por la alteración hidrotermal asociada a filones de Ba-(Pb-Zn), es evaluado utilizando elementos inmóviles como monitores. Por correlación, se comprueba que existe transferencia de Al, utilizandose Zr como elemento de referencia.

Key words: *hydrothermal alteration, granite metasomatism, Aluminium, Ba-(Pb-Zn) ore, Linares.*

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Introduction

Preserved metasomatism in alteration envelopes are important not only because of the information that it provides on water/rock interaction degree and composition of the hydrothermal fluid but also because its potential effects on fluid chemistry and element transport. For these reasons, accurate calculations of mass transfers are of great importance in studies where precise geochemical data are required (e.g. structural and hydrogeological studies for HLW disposal).

The basic argument for calculations of metasomatic gains and losses is that some components (e.g. Al, Ti, Zr, Y and Nb) are likely to have been immobile in the alteration processes (Gresens, 1967). In granitic rocks, Al is widely used because is a major constituent of the rock, and therefore more precisely determined. But as it is shown in this contribution, Al may experience some mobility in altered granites, being necessary to verify its 'immobility' prior to the gains-losses calculations to avoid large errors.

Sampling

11 Samples of altered adamellites of the Linares massif (Linares-La Carolina Pb-ore field, southeastern border of the Central-Iberian Zone) were collected in situ. The sampling was carried out in a profile of 10 m at the level 11 (at 400 m depth) of El Cobre lode (South branch). The surveyed profile displays argillic-propylitic to propylitic assemblages, the phyllic and argillic (s.s) assemblages being absent. The argillic-propylitic assemblage (sericite ± chlorite ± kaolinite ± calcite ± pyrite ± quartz) develops on the first 5-6 meter from the vein. The alkali metasomatism assemblage (K-feldspar ± albite ± muscovite) overprints that argillic-propylitic assemblage. A weak propylitic assemblage (chlorite ± sericite with traces of kaolinite) appears farther than 5-6 meter from the vein. Alkali metasomatism is practically absent from that distance. (Lillo, 1992).

10 Unaltered/less altered samples of the adamellite were collected from "fresh" outcrops at nearby places of the location of the altered samples.

XRF data on whole-rock geochemistry of the hydrothermally altered rocks and less altered rocks are presented in table 1.

Whole-rock geochemistry: mass transfers

Calculation of the changes in chemical composition accompanying the hydrothermal alteration of host rocks requires that: a) the range of possible fresh-rock compositions (protoliths) is known, b) the altered sample analyses must be corrected for diluting effects of mineralisation or for the concentrating effects of net mass leaching.

In this study, the range of potential protoliths is well constrained from ten analyses of unaltered/less altered samples from the Linares granitoid.

Immobile elements are used to correct the data of altered samples for dilution or concentration effects. Commonly, the normalisation factor is the ratio of equivalent masses estimated from immobile element ratios before and after alteration (Grant, 1986).

Immobile elements are recognised by constant concentration ratios throughout an alteration sequence or profile, despite the fact that the elements occur in different minerals (Gresens, 1967)

The composition of altered samples versus the composition of unaltered/less altered samples have been plotted in Fig. 1, where a isocon line or line of isoconcentration (Grant, 1986) for Al has been drawn. Ti, Th, Y, Zr, and Nb (usually considered as immobile, eg. McLean and Kranidiotis, 1987) show displacements from that isocon reflecting that Al is not truly immobile whereas Ti, Th, Y, Zr and Nb are relatively well correlated.

The observed poor correlation between Al and these elements can not be explained by original magmatic fractionation (c.f. McLean, 1990) as unaltered samples (collected from different locations) display grouped distributions (Fig. 2).

Al may be mobile to some degree

(e.g. Anderson and Burnham, 1983; Kerrick, 1990) but addition of Al to alteration envelopes in granites has been a scarcely reported in the literature (e.g. Bölke, 1989).

In this study, Zr was selected as the normalising component for mass transfer calculations because is highly immobile (even more than Ti, MacLean and Kranidiotis, 1987), abundant and is more accurately analysed by the X-ray fluorescence method than other trace elements.

Gains and losses may be calculated by the expression (Gresens, 1967; Grant, 1986):

Gain/Loss = Mean $C^{O}zr$ / $C^{A}zr$ * $C^{A}i$ - mean $C^{O}i$

where COzr and CAzr are concentrations of Zr in the protolith and the altered sample respectively; $C^{O}i$ and $C^{A}i$ are the concentration of the oxide or element i in the protolith and the altered sample respectively. The mass transfer is given in grams per 100 grams of protolith (oxides) or milligrams per kilogram of protolith (trace elements).

Table 2 shows gains and losses normalised to Zr. For comparison, gains and losses normalised to Al are presented in table 3. As it may be noted from the tables, the use of Zr or Al as normalising component may change significantly the results on Na , Ba and Zn transfers, even in some case (e.g. Na) with negative sign ("from loss to gain").

Thus, in the El Cobre alteration halo, Si, Al, K, Na, Rb and Pb increase from the vein in the first five meter of the profile. In that zone, argillic-propylitic assemblage occurs, overprinted by a late formation of K-feldspar and albite. On the 7th m., the gains fall abruptly to values close to those of the unaltered samples. Ba shows a scattered distribution in the profile. Ca and Sr show a regular depletion toward the vein.

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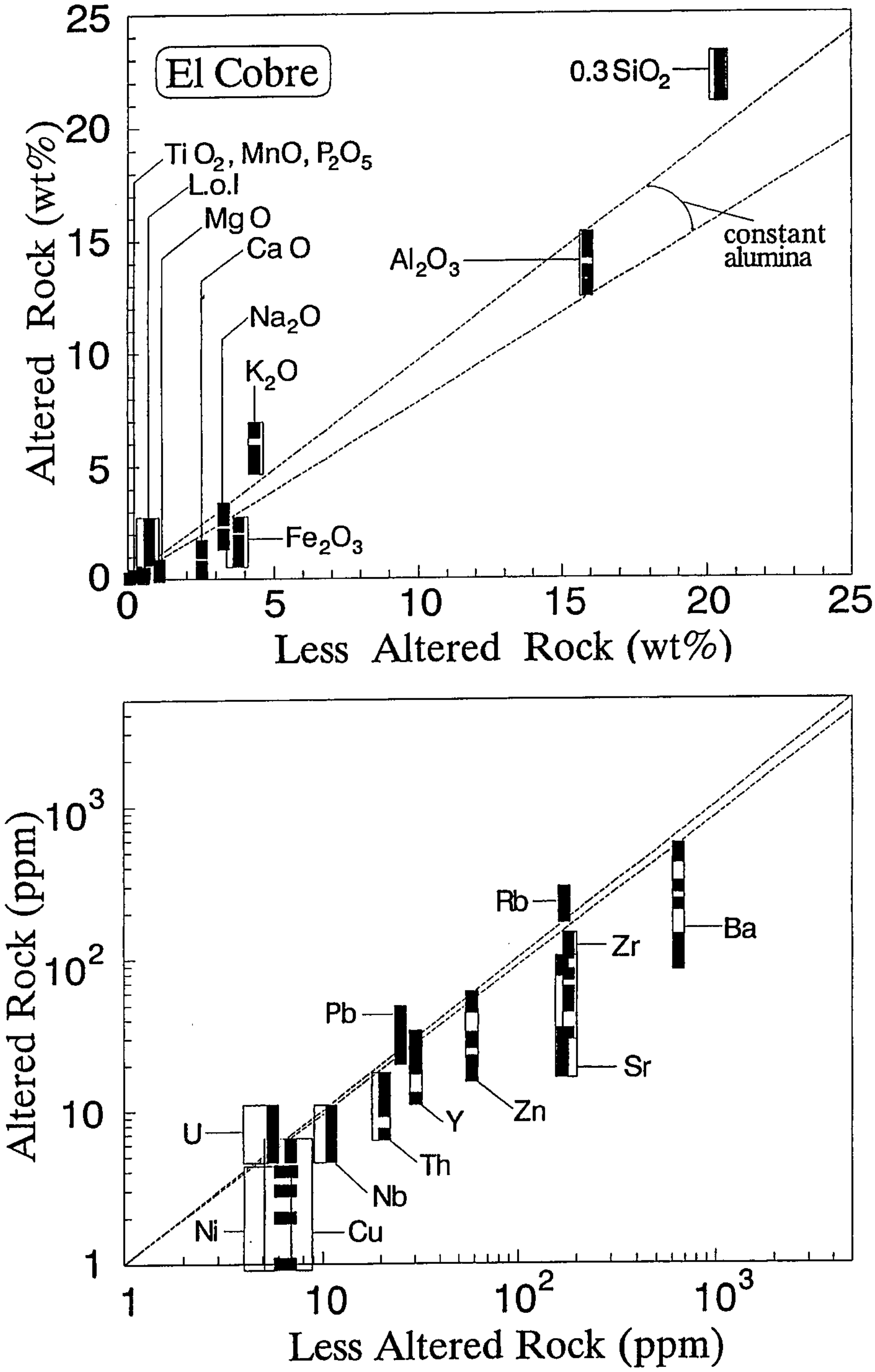

Fig. 1.- Mass transfers in El Cobre Wall-rocks (Linares granite). Isocon line for alumina is drawn for reference (based on Grant, 1986). Areas represent the compositional range for the analysed samples (altered and unaltered).

Fig. 1.- Tranferencias de masas en las rocas de caja de El Cobre (granito de Linares). Se ha dibujado la línea isocona de la alúmina como referencia (basado en Grant, 1986). Las áreas representan el rango composicional de las muestras analizadas (alteradas e inalteradas)

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Unaltered				Altered granite										
range	std	mean	mts	0,50	1,00	2,00	3,00	4,00	5,00	6,00	7,00	8,00	9,00	10,00
66-94-69.00	0,70	68,15	SiO2	76,03	73,19	73,71	75,44	76,66	76,07	76,75	72,37	71,08	71,43	71,50
0.47-0.57	0,03	0,53	TiO2	0,18	0,14	0,23	0,11	0,12	0,05	0,09	0,24	0,26	0,27	0,25
15.63-16.02	0,26	15,90	Al2O3	12,94	13,53	14,40	13,57	12,73	13,52	12,87	15,09	14,63	14,93	14,99
3.37-4.11	0,19	3,78	Fe2O3	1,71	1,25	1,43	1,04	1,46	0,80	1,20	2,47	2,41	2,51	2,35
0.05-0.06	0,00	0,06	MnO	0,03	0,05	0,02	0,03	0,04	0,03	0,03	0,05	0,04	0,05	0,04
1.01-1.17	0,05	1,08	MgO	0,32	0,26	0,26	0,23	0,22	0,13	0,21	0,56	0,48	0,59	0,61
2.34-2.66	0,12	2,52	CaO	0,33	1,19	0,25	0,55	0,56	0,44	0,41	1,47	1,45	1,27	1,26
3.16-3.49	0,09	3,27	Na2O	1,98	1,76	1,56	1,92	2,64	3,07	2,80	3,15	3,06	2,83	3,12
4.11-4.63	0,17	4,32	K2O	5,67	6,59	6,51	6,68	5,17	5,39	5,57	4,91	5,14	5,11	5,13
0.20-0.22	0,01	0,21	P2O5	0,12	0,12	0,16	0,13	0,15	0,18	0,12	0,14	0,15	0,17	0,16
1.09-0.30	0,24	0,73	L.o.I	1,09	2,50	2,04	2,20	1,10	1,37	1,09	1,09	0,89	1,50	1,29
			Total	100,41	100,59	100,56	101,90	100,84	101,05	101,15	101,52	99,59	100,66	100,69
28-34	2,93	30,00	Co	30,00	20,00	25,00	30,00	24,00	21,00	28,00	24,00	25,00	23,00	28,00
4-7	0,94	6,10	Ni	3,00	2,00	3,00	3,00	2,00	1,00	2,00	4,00	2,00	2,00	4,00
5-9	1,51	6,90	Cu	1,00	3,00	2,00	2,00	2,00	6,00	3,00	5,00	4,00	3,00	4,00
54-62	2,83	58,30	Zn	28,00	21,00	20,00	17,00	30,00	17,00	19,00	52,00	52,00	48,00	55,00
163-180	5,14	173,60	Rb	218,00	212,00	197,00	226,00	238,00	271,00	230,00	200,00	188,00	199,00	195,00
154-202	14,59	170,20	Sr	20,00	31,00	32,00	28,00	23,00	18,00	21,00	95,00	89,00	83,00	88,00
28-32	1,34	30,00	Y	26,00	19,00	31,00	22,00	19,00	12,00	23,00	30,00	30,00	27,00	25,00
171-199	9,08	182,60	Zr	78,00	60,00	107,00	54,00	49,00	32,00	48,00	135,00	114,00	132,00	116,00
9-12	1,04	11,10	Nb	9,00	6,00	8,00	5,00	7,00	7,00	7,00	9,00	9,00	10,00	9,00
599-681	22,34	647,90	Ba	131,00	224,00	292,00	224,00	109,00	106,00	91,00	455,00	459,00	516,00	459,00
24-31	1,95	25,30	Pb	39,00	26,00	22,00	27,00	25,00	45,00	29,00	32,00	39,00	30,00	33,00
18-22	1,22	20,90	Th	11,00	10,00	12,00	10,00	10,00	7,00	10,00	16,00	14,00	15,00	15,00
4-6	0,80	5,60	U	8,00	8,00	5,00	7,00	8,00	10,00	9,00	8,00	6,00	7,00	8,00

Table 1. Whole-rock compositional data of unaltered and altered samples from El Cobre lode (Linares granite, Jaén)

Tabla 1.- Datos composicionales de roca total en muestras inalteradas y alteradas de el filón El Cobre (granito de Linares, Jaén)

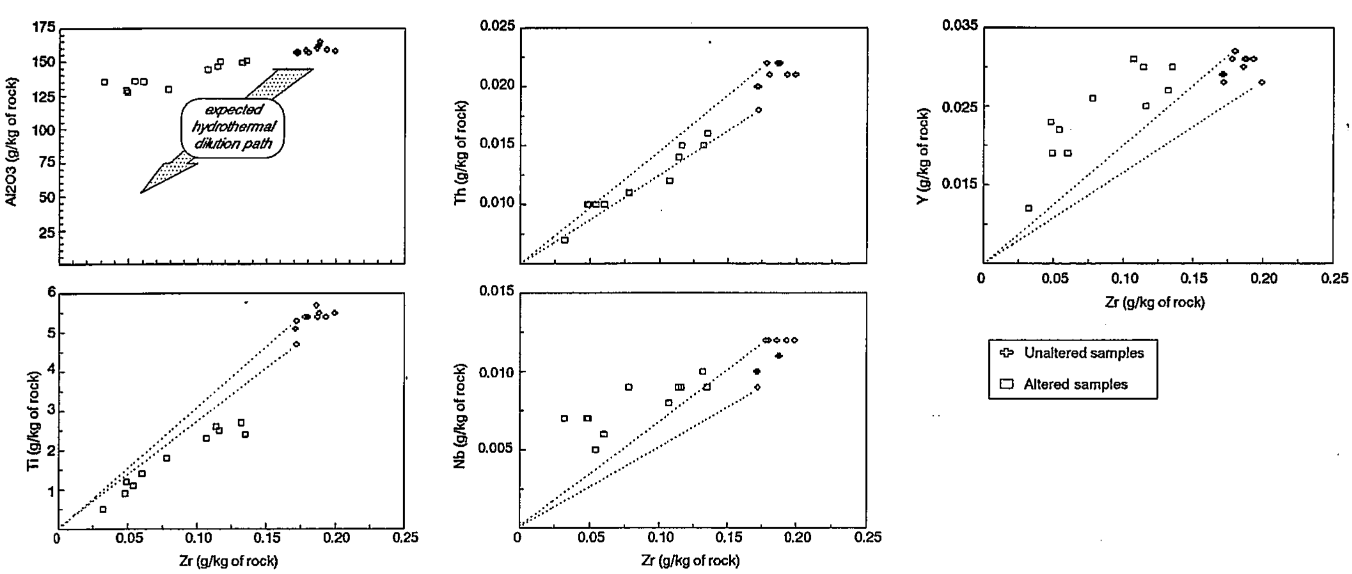

Fig. 2.- Test for immobile elements in altered samples from El Cobre wall-rocks (Linares granite). Dotted lines represent the expected path caused by hydrothermal dilution.

Fig. 2.- Test para elementos no móviles en muestras de la roca de caja de El Cobre (granito de Linares). Las líneas de puntos representan la tendencia esperable por dilución hidrotermal.

GAINS AND LOSSES (Relative to the only isocon and the concentration prior to alteration)											
mts	0,50	1,00	2,00	3,00	4,00	5,00	6,00	7,00	8,00	9,00	1,0023
SiO2	109,84	154,59	57,64	186,95	217,53	365,92	223,82	29,74	45,70	30,66	44,40
TiO2	(0,11)	(0,10)	(0,14)	(0,16)	(0,08)	(0,24)	(0,19)	(0,21)	(0,11)	(0,16)	(0,14)
Al2O3	14,39	25,28	8,67	29,99	31,54	61,25	33,06	4,51	7,53	4,75	7,70
Fe2O3	0,22	0,02	(1,34)	(0,26)	1,66	0,79	0,79	(0,44)	0,08	(0,31)	(0,08)
MnO	0,01	0,09	(0,03)	0,04	0,09	0,11	0,05	0,01	0,00	0,01	0,00
MgO	(0,33)	(0,29)	(0,64)	(0,30)	(0,26)	(0,34)	(0,28)	(0,32)	(0,31)	(0,26)	(0,12)
CaO	(1,75)	1,10	(2,09)	(0,66)	(0,43)	(0,01)	(0,96)	(0,53)	(0,20)	(0,76)	(0,54)
Na2O	1,37	2,09	(0,61)	3,22	6,57	14,25	7,38	0,99	1,63	0,64	1,64
K2O	8,95	15,74	6,79	18,27	14,95	26,44	16,87	2,32	3,91	2,75	3,76
P2O5	0,07	0,16	0,06	0,23	0,35	0,82	0,25	(0,02)	0,03	0,03	0,04
L.o.I	1,82	6,88	2,75	6,71	3,37	7,09	3,42	0,74	0,70	1,35	1,30
NFactor	2,34	3,04	1,71	3,38	3,73	5,71	3,80	1,35	1,60	1,38	1,57
Co	40,23	30,87	12,66	71,44	59,44	89,83	76,52	2,46	10,04	1,82	14,08
Ni	0,92	(0,01)	(0,98)	4,04	1,35	(0,39)	1,51	(0,69)	(2,90)	(3,33)	0,20
Cu	(4,56)	2,23	(3,49)	(0,14)	0,55	27,34	4,51	(0,14)	(0,49)	(2,75)	(0,60)
Zn	7,25	5,61	(24,17)	(0,81)	53,50	38,71	13,98	12,03	24,99	8,10	28,28
Rb	336,74	471,59	162,59	590,61	713,31	1.372,79	701,36	96,92	127,53	101,68	133,36
Sr	(123,38)	(75,86)	(115,59)	(75,52)	(84,49)	(67,49)	(90,31)	(41,70)	(27,64)	(55,38)	(31,68)
Y	30,87	27,82	22,90	44,39	40,80	38,48	57,50	10,58	18,05	7,35	9,35
Zr	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Nb	9,97	7,16	2,55	5,81	14,99	28,84	15,53	1,07	3,32	2,73	3,07
Ba	(341,23)	33,81	(149,59)	109,55	(241,71)	(43,04)	(301,72)	(32,47)	87,31	65,90	74,63
Pb	66,00	53,83	12,24	66,00	67,86	231,48	85,02	17,98	37,17	16,20	26,65
Th	4,85	9,53	(0,42)	12,91	16,37	19,04	17,14	0,74	1,52	(0,15)	2,71
U	13,13	18,75	2,93	18,07	24,21	51,46	28,64	5,22	4,01	4,08	6,99

Table 2. Gains and losses normalised to Zr of altered samples from El Cobre lode (Linares granite)
Tabla 2.- Ganancias y pérdidas normalizadas a Zr de muestras alteradas de el filón El Cobre (granito de Linares)

GAINS AND LOSSES (Relative to the only isocon and the concentration prior to alteration)											
mts	0,50	1,00	2,00	3,00	4,00	5,00	6,00	7,00	8,00	9,00	10,00
SiO2	25,27	17,86	13,24	20,24	27,60	21,31	26,67	8,10	9,10	7,92	7,69
TiO2	(0,31)	(0,37)	(0,28)	(0,40)	(0,38)	(0,47)	(0,42)	(0,28)	(0,25)	(0,24)	(0,26)
Al2O3	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Fe2O3	(1,68)	(2,31)	(2,20)	(2,56)	(1,96)	(2,84)	(2,30)	(1,18)	(1,16)	(1,11)	(1,29)
MnO	(0,02)	0,00	(0,04)	(0,02)	(0,01)	(0,02)	(0,02)	(0,01)	(0,02)	(0,01)	(0,02)
MgO	(0,69)	(0,77)	(0,79)	(0,81)	(0,81)	(0,93)	(0,82)	(0,49)	(0,56)	(0,45)	(0,43)
CaO	(2,11)	(1,12)	(2,24)	(1,88)	(1,82)	(2,00)	(2,01)	(0,97)	(0,94)	(1,17)	(1,18)
Na2O	(0,84)	(1,20)	(1,55)	(1,02)	0,03	0,34	0,19	0,05	0,06	(0,26)	0,04
K2O	2,65	3,42	2,87	3,51	2,14	2,02	2,56	0,85	1,27	1,12	1,12
P2O5	(0,06)	(0,07)	(0,03)	(0,06)	(0,02)	0,00	(0,06)	(0,06)	(0,05)	(0,03)	(0,04)
L.o.I	0,61	2,21	1,52	1,85	0,64	0,88	0,62	0,42	0,24	0,87	0,64
NFactor	1,23	1,18	1,10	1,17	1,25	1,18	1,24	1,05	1,09	1,06	1,06
Co	6,86	(6,50)	(2,40)	5,15	(0,02)	(5,30)	4,59	(4,71)	(2,83)	(5,51)	(0,30)
Ni	(2,41)	(3,75)	(2,79)	(2,58)	(3,60)	(4,92)	(3,63)	(1,89)	(3,93)	(3,97)	(1,86)
Cu	(5,67)	(3,37)	(4,69)	(4,56)	(4,40)	0,16	(3,19)	(1,63)	(2,55)	(3,71)	(2,66)
Zn	(23,90)	(33,62)	(36,22)	(38,38)	(20,83)	(38,31)	(34,83)	(3,51)	(1,79)	(7,18)	0,04
Rb	94,27	75,54	43,92	91,20	123,67	145,11	110,55	37,14	30,72	38,33	33,24
Sr	(145,63)	(133,77)	(134,87)	(137,39)	(141,47)	(149,03)	(144,26)	(70,10)	(73,47)	(81,81)	(76,86)
Y	1,95	(7,67)	4,23	(4,22)	(6,27)	(15,89)	(1,59)	1,61	2,60	(1,25)	(3,48)
Zr	(86,76)	(112,09)	(64,45)	(119,33)	(121,40)	(144,97)	(123,30)	(40,35)	(58,70)	(42,02)	(59,56)
Nb	(0,04)	(4,05)	(2,27)	(5,24)	(2,36)	(2,87)	(2,45)	(1,62)	(1,32)	(0,45)	(1,55)
Ba	(486,93)	(384,66)	(325,48)	(385,44)	(511,76)	(523,24)	(535,48)	(168,48)	(149,06)	(98,38)	(161,04)
Pb	22,62	5,25	(1,01)	6,34	5,93	27,62	10,53	8,42	17,09	6,65	9,70
Th	(7,38)	(9,15)	(7,65)	(9,18)	(8,41)	(12,67)	(8,55)	(4,04)	(5,68)	(4,93)	(4,99)
U	4,23	3,80	(0,08)	2,60	4,39	6,16	5,52	2,83	0,92	1,85	2,89

Table 3. Gains and losses normalised to Al of altered samples from El Cobre lode (Linares granite)
Tabla 3.- Ganancias y pérdidas normalizadas a Al de muestras alteradas del filón El Cobre (granito de Linares)