

# Geochemistry of metapelitic rocks from the Garmichay Area, East Azerbaijan, NW Iran; protolith nature and whole rock control on metamorphic mineral assemblages

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## Abstract

The protoliths of metamorphosed argillaceous rocks from the Garmichay area in the East Azerbaijan province of NW Iran were clay-rich sediments of reworked nature, originating most likely from an andesite to andesite-basalt source and deposited in an active continental margin tectonic setting. The protoliths of the Garmichay metapelites experienced low to moderate chemical weathering. Andalusite, cordierite, biotite, and muscovite are produced due to metamorphism under low-pressure and medium-temperature conditions. Cordierite throughout the whole assemblages is altered to the pseudomorphs pinite. Some rock samples contain both andalusite and altered cordierite as porphyroblasts, whereas others contain only andalusite or altered cordierite. Pressure and temperature estimates indicate that pressure for metamorphism was in the range 1-2.5 kbar with temperature between 500-600°C. Major oxides abundance show similar values in all analyzed samples, while concentration of some minor elements, especially zinc, show meaningful differences in rocks with different metamorphic mineral assemblages. The variations in the abundance of these minor elements may have played important role in the control of the mineral assemblages present.

**Keywords:** Chemical Weathering, Metamorphism, Metapelite, Mineral Assemblage, NW Iran, Protolith.

## Introduction

The whole rock geochemistry of clay-rich rocks and their metamorphic equivalents are frequently used to study the provenance, tectonic setting, and palaeoweathering of the geological environment (e.g. Nesbitt and Young, 1982; Taylor and McLennan, 1985; Wronkiewicz and Condie, 1987; Zhang *et al.*, 1998; Long *et al.*, 2008).

Metamorphosed argillaceous (metapelitic) rocks in NW Iran appear as different types of pelitic schists. The main occurrences of these rocks are in the Takab (Saki, 2010; Saki *et al.*, 2012) and Garmichay areas. The rocks in both areas are associated with un-metamorphosed sedimentary units with Palaeozoic (Cambrian to Carboniferous) and younger ages. There are no geochronological data on the age of these metapelites, but considering the stratigraphical relations and the fact that the associated Palaeozoic rocks are not metamorphosed, the age of the metapelites in both Takab and Garmichay areas is considered to be Precambrian (Behruzi *et al.*, 1992; Saki, 2010; Saki *et al.*, 2012).

Jamshidi Badr *et al.* (2013) reported 543±6 Ma and 537±8 Ma ages for two types of granitoids from the Soursat Mountain in the Takab area. Hassanzadeh *et al.* (2008) obtained zircon U/Pb

ages of ~548 and ~568 Ma for Moghanlou and Mahnesan granitoids from the Takab area, respectively. Moazzen *et al.* (2013), using SHRIMP U/Pb dating on zircons from the migmatites in the Takab area, found ages of ~29 to 25.7 Ma for partial melting. They consider this for extended period of partial melting.

The much older ages of ~2900 Ma are considered as very old zircon cores (Moazzen *et al.*, 2013). Shafaii Moghadam *et al.* (2016) also studied the migmatites and suggested that rim growth and formation of new zircons in the leucosomes of migmatites were associated with partial melting at 28–25 Ma. These ages are comparable with results published by Moazzen *et al.* (2013). Metapelites in the Garmichay area appear in a small tectonic window.

In this contribution, we try to provide information on the geochemistry of these metapelites in order to furnish suitable ground for further investigations. This is the first report on geochemistry of pelitic rocks from the Garmichay area. We will discuss some aspects of the rocks such as nature of the protolith, their weathering and deposition conditions, possible tectonic setting of the sediments, their metamorphic conditions, and factors controlling metamorphic mineral assemblages of these rocks.

### Geological setting

Based on similarities in sedimentation, magmatism, metamorphism, and deformation, the Iranian crust is divided into several litho-tectonic units (Stöcklin, 1968; Eftekharnjad, 1981). Figure 1 shows the geological subdivision of Iran after Stöcklin (1968). The study area is a part of the Central Iran/ Alborz-Azerbaijan subdivision.

The main rock types in the study area are andalusite schist, cordierite schist, biotite-muscovite schist (Fig. 2), marble, granitoid (Fig. 3) and rare metabasites. Metapelites are observed in two main areas, at the eastern side of the Garmichay River and between Neibaghi and Molk villages (Fig. 2). Marbles and metamorphosed calc-silicate rocks overlie the metapelites in this area. Rhyolitic and dacitic lavas (Fig. 3) of Oligocene age overlie all of the metamorphic rocks. Around the Siahmansour village (Fig. 2), metapelites are overlain unconformably by Cretaceous limestone. Two types of granitoids occur in this area. The first type is a pinkish granite, synchronously metamorphosed with the pelitic rocks and the second, younger granite which cuts all units except the upper rhyolite. Miocene polymictic conglomerate has considerable outcrop in the area (Fig. 2).

### Petrography of the metapelites

Metapelites around Siahmansour village (Fig. 2) exhibit a well-developed schistosity, with

andalusite porphyroblasts clearly evident in hand specimen (Fig. 3). The main mineral assemblage in these rocks is And+Bt+Qz (mineral name abbreviations after Whitney and Evans, 2010). Andalusite is the single porphyroblastic mineral in these assemblages with sizes ranging between 0.5 to 2 mm. In some samples, biotite occurs as inclusions within the andalusite. The dominant texture of these rocks is porphyro-lepidoblastic, with parallel alignment of biotite and muscovite defining the schistosity. The minor mineral phases include opaque minerals, apatite, and tourmaline.

Metapelites near the Neibaghi, Molk, and Tajaragh villages, east of the Garmichay River (Fig. 2), occur as alternating layers with the more psammitic rocks containing both highly altered cordierite (pseudomorphed by pinitite) together with andalusite porphyroblasts. Most of the cordierite is highly altered and only a small percentage of fresh relicts of cordierite remain. Five main mineral assemblages were distinguished in these rocks including (plus non-KFAMSH minerals such as plagioclase and oxide minerals):

- (1) Bt+Ms+Chl+Qz
- (2) Bt+Ms+Qz
- (3) Crd+Bt+Ms+Chl+Qz
- (4) And+Bt+Ms+Qz
- (5) And+Crd+Bt+Ms+Qz

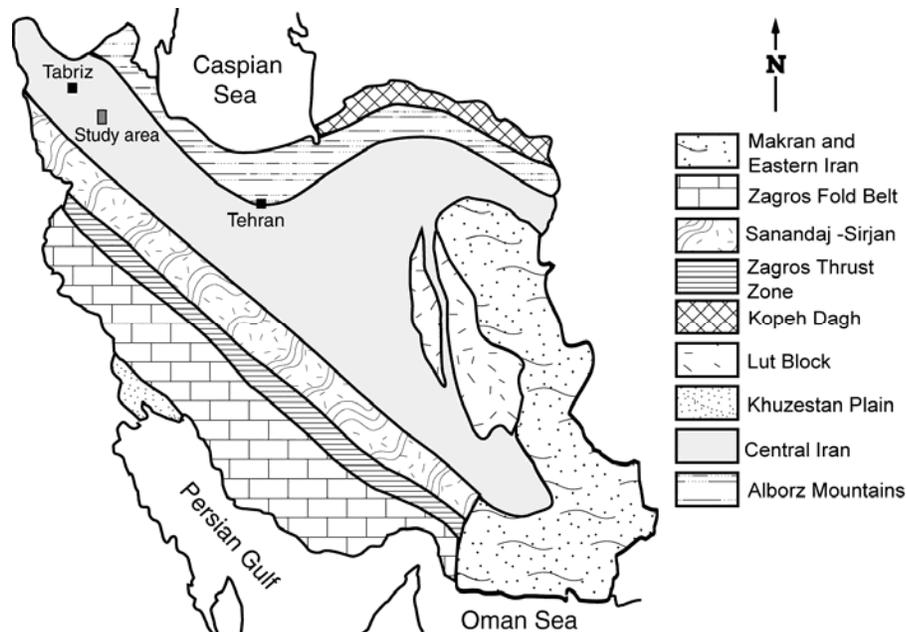


Figure 1. Geological subdivision of Iran (after Stöcklin, 1968) and the location of the study area

The dominant textures identified in these rocks are porphyroblastic in which pseudomorphs of cordierite and andalusite make up the porphyroblasts and lepidoblastic in which muscovite and biotite clearly define the rocks' schistosity. Some samples, especially those from the Tajaragh area, do not contain andalusite and pseudomorphed cordierite and are simply biotite-muscovite schists.

In most rock samples from east of the Garmichay River, pinitized cordierite appears as porphyroblasts with an absence of andalusite. The minor phases are

tourmaline, opaque minerals, apatite, plagioclase, and zircon. Andalusite and pseudomorphed cordierite, wrapped with the main foliation, are regarded as pre-deformational minerals. In brief, metapelites of the Garmichay area can be divided into four main groups called (i) metapelites lacking both cordierite and andalusite, (ii) metapelites containing only pseudomorphed cordierite porphyroblasts, (iii) metapelites containing only andalusite porphyroblasts, and (iv) metapelites containing both pseudomorphed cordierite and andalusite porphyroblasts (Fig. 4).

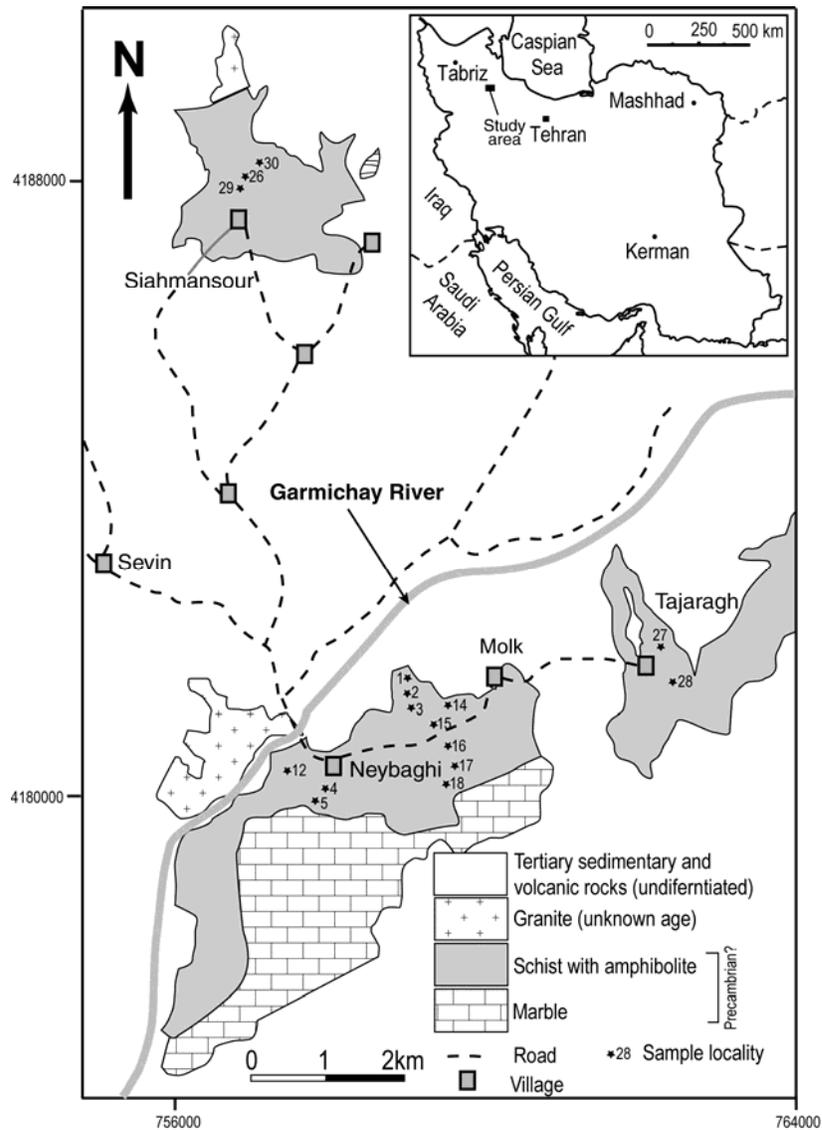


Figure 2. Simplified geological map of the Garmichay area

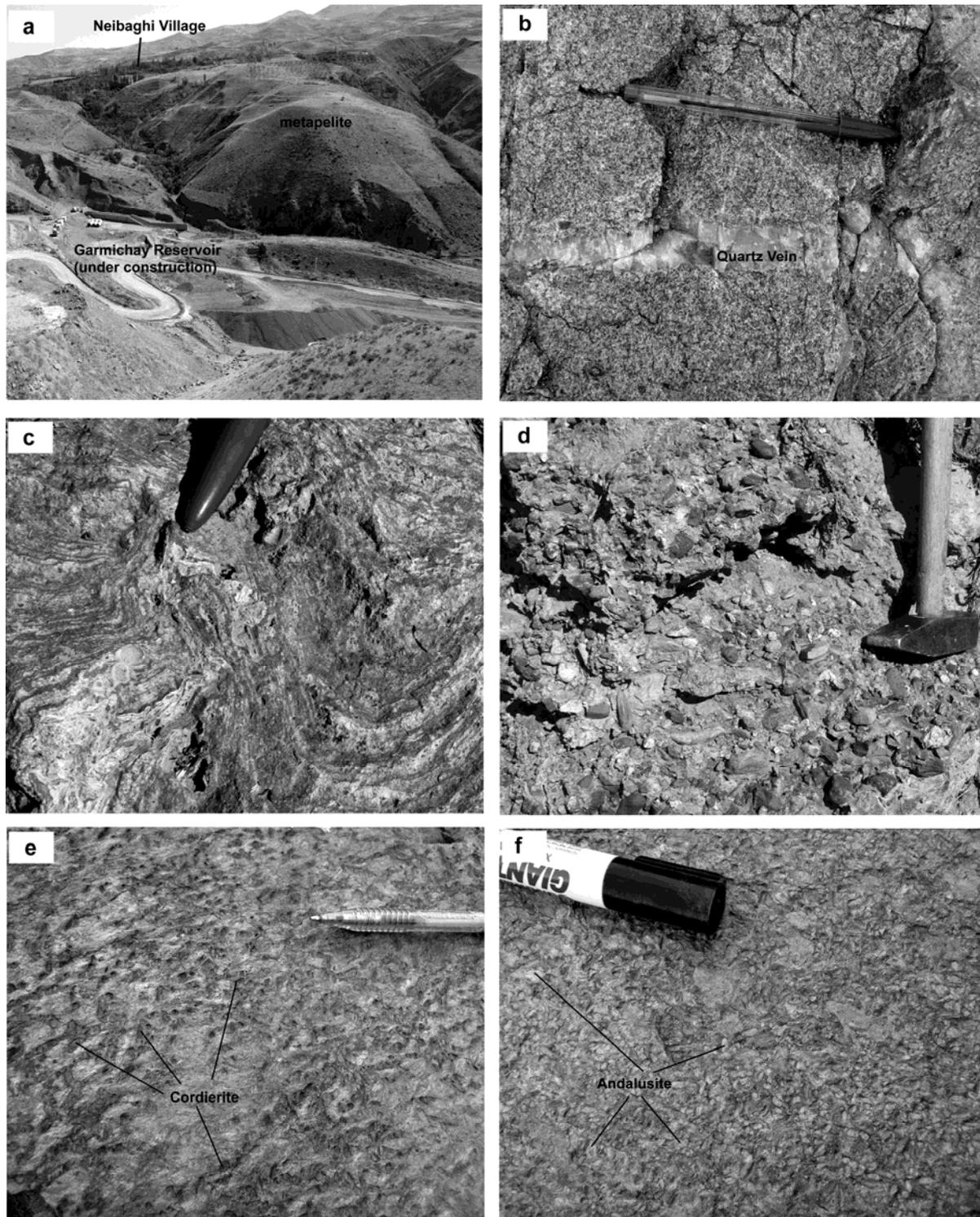


Figure 3. a) Outcrop of the metapelites close to the Neibaghi village, b) Outcrop of granitoids with quartz veins, c) Flow structure in ignimbrite, d) Conglomerate with igneous and metamorphic rock fragments, e) Cordierite-bearing metapelite, f) Andalusite-bearing metapelite

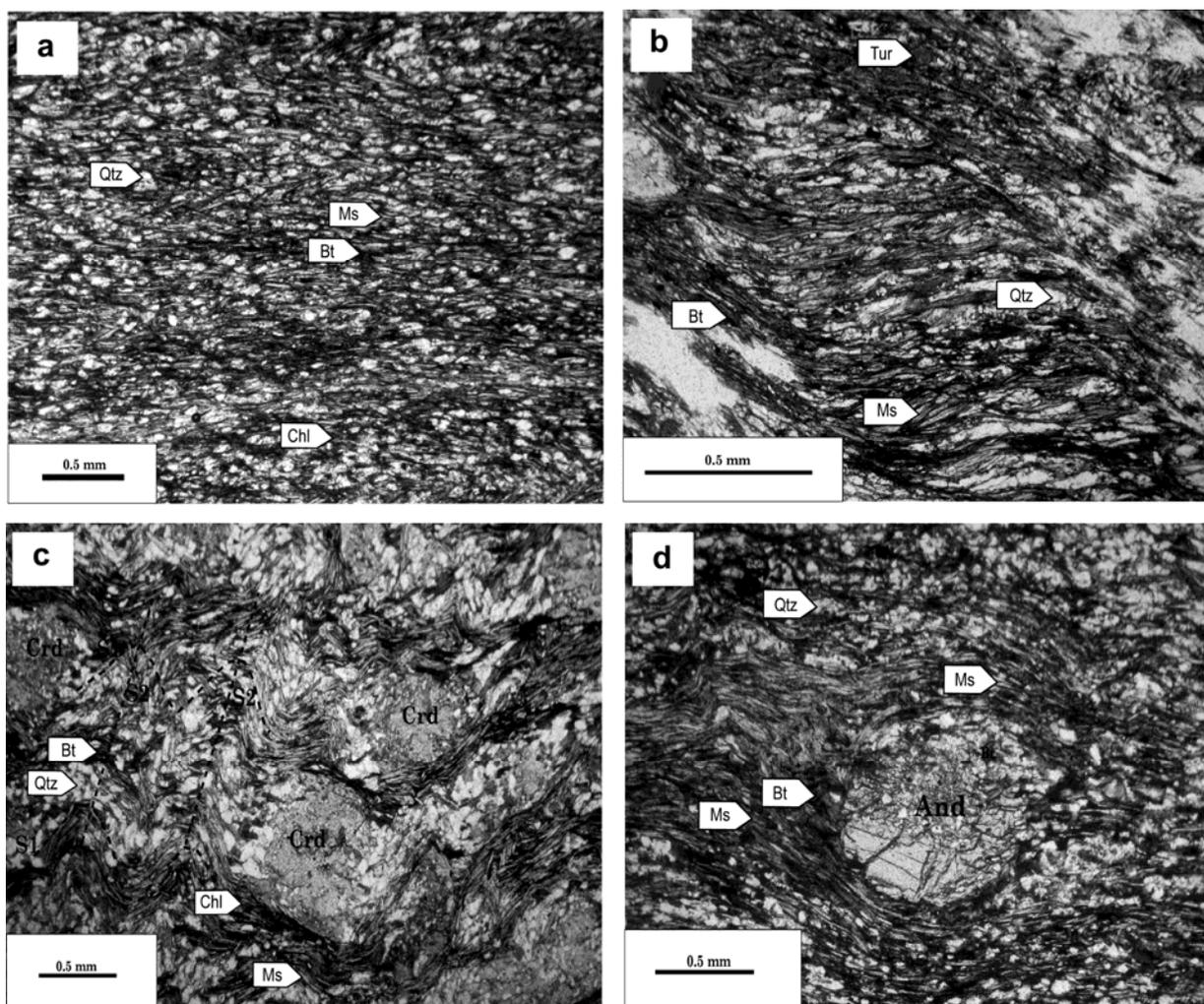


Figure 4. a) Metapelitic rock lacking both cordierite and andalusite porphyroblasts, b) Deformation of former foliation in pelitic schist, c) Ex-cordierite porphyroblasts altered to pinite,  $S_1$  and  $S_2$  foliations are shown. Andalusite porphyroblast wrapped by the main foliation ( $S_2$ ).

Table 1 lists the mineral assemblages observed in the studied rocks. Differences in mineral paragenesis in the Garmichay metapelites can be attributed to either difference in the whole rock chemistry of the pelitic rocks; differences in the pressure and temperature of the metamorphic conditions, or both.

#### Whole rock geochemistry

Ten optically well-defined representative samples from the Garmichay metapelites were analyzed for major, trace, and rare earth elements. Analyses were performed in ALS Chemex, Canada. Whole rock major element abundances were determined by inductively coupled plasma- atomic emission spectrometry (ICP-AES) with a detection limit of

0.01%.

Following lithium metaborate fusion, rare earth and trace elements were determined by inductively coupled plasma-mass spectrometry (ICP-MS) with a detection limit of 0.01 ppm to 2 ppm. The analytical error for most elements is less than 2%. Details of the chemical procedures are accessible at [www.alschemex.com](http://www.alschemex.com). The results are tabulated in Tables 2 and 3. The composition of Post Archaean Australian Shale (PAAS, Taylor and McLennan, 1985) is provided for comparison.

#### Variation of Major Oxides

The metapelitic rocks of the Garmichay have high  $\text{SiO}_2$  (60.5 to 67.5 wt%) and  $\text{Al}_2\text{O}_3$  (14 to 18wt%) contents.

Table 1. Mineral assemblages of metapelitic rocks from the Garmichay area, NW Iran.

Sample No.	UTM (38S)		And	ex-Crd	Bt	Ms	Qz	Chl	Ap	Tur	Pl
1B	759151	4181470			*	*	*				
3A	759178	4181425			*	*	*	*	*	*	*
3C	759178	4181425	*	*	*	*	*	*		*	
4B	758099	4180132	*	*	*	*	*	*		*	
4B2	758099	4180132		*	*	*	*	*		*	
6D	757995	4180071		*	*	*	*	*		*	
9A1	Very close to sample 1B			*	*	*	*	*		*	
9A3	"				*	*	*	*		*	
9A4	"				*	*	*	*		*	*
9A5	"				*	*	*				
9A6	"				*	*	*				
9B2	"				*	*	*				
12A	757595	4180686			*	*	*	*		*	
14B	759628	4181618			*	*	*	*		*	
15B	759480	4180775	*	*	*	*	*	*			
16B	759408	4180661	*	*	*	*	*	*		*	
16C	759408	4180661	*	*	*	*	*	*		*	
16D	759408	4180661			*	*	*	*		*	*
16E	759408	4180661	*	*	*	*	*	*		*	
17B	759533	4180460		*	*	*	*	*		*	
17C	759533	4180460		*	*	*	*			*	
17G	759533	4180460		*	*	*	*			*	
17C	759533	4180460		*	*	*	*	*		*	
26	756773	4187631	*		*	*	*	*		*	

Table 2. Major oxides and calculated chemical indices for Garmichay metapelites.

	3C	15B	16B	16E	17B	17G	26A	26C	26D	26J	Min	Max	Ave	PA
	Crd-	Crd-	Crd-	Crd-	Crd	Crd	And	And	And	And				
Wt%														
SiO <sub>2</sub>	61.2	62.4	61.2	60.5	67.5	61.8	61.5	63	65.6	61.1	60.5	67.5	62.5	62.8
TiO <sub>2</sub>	0.76	0.79	0.75	0.76	0.64	0.79	0.86	0.84	0.72	0.86	0.64	0.86	0.78	1
Al <sub>2</sub> O <sub>3</sub>	17.3	16.4	17.0	18.1	14.0	17.2	17.4	17.7	14.6	18	14.0	18.1	16.8	18.9
Fe <sub>2</sub> O <sub>3</sub> <sup>T</sup>	6.74	6.49	6.67	6.23	5.54	6.49	6.5	5.95	6.34	6.09	5.54	6.74	6.3	6.5
MgO	3.01	2.93	2.89	2.94	2.45	2.86	2.81	2.73	2.31	2.64	2.31	3.01	2.76	2.2
CaO	0.49	0.48	0.51	0.43	0.68	0.41	0.53	0.5	0.67	0.49	0.41	0.68	0.52	1.3
Na <sub>2</sub> O	2	2.22	1.58	1.3	2.43	1.24	0.83	1.87	2.14	1.62	0.83	2.43	1.72	1.2
K <sub>2</sub> O	3.57	3.39	3.92	4.06	2.81	4.32	4.5	3.98	3.11	4.31	2.81	4.5	3.8	3.8
MnO	0.05	0.04	0.04	0.04	0.05	0.06	0.03	0.03	0.03	0.03	0.03	0.06	0.04	0.1
P <sub>2</sub> O <sub>5</sub>	0.12	0.16	0.15	0.16	0.1	0.11	0.17	0.2	0.15	0.23	0.1	0.23	0.16	0.16
LOI	3.11	2.91	3.63	3.8	2.12	3.01	3.18	3.11	2.62	3.2	-	-	-	n.d.
Total	98.4	98.3	98.4	98.3	98.4	98.3	98.4	99.9	98.3	98.6	-	-	-	97.8
SiO <sub>2</sub> /	3.53	3.79	3.59	3.34	4.8	3.58	3.52	3.56	4.48	3.39	3.34	4.8	3.72	3.32
K <sub>2</sub> O/	1.79	1.53	2.48	3.12	1.16	3.48	5.42	2.13	1.45	2.60	1.16	5.42	2.2	3.18
K <sub>2</sub> O+	5.57	5.61	5.5	5.36	5.24	5.56	5.33	5.85	5.25	5.93	5.24	5.93	5.52	5.01
ICV	0.96	0.99	0.96	0.87	1.04	0.94	0.92	0.9	1.05	0.89	0.87	1.05	0.95	0.85
CIA	68.3	66.5	68.7	71.1	63	69.8	71	68.2	64.3	68.5	63	71.1	67.9	69
CIW	80.6	78.2	83.1	85.9	73	86.2	88.6	81.7	75.4	83.4	73	88.6	81.6	81.5
DF1	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DF2	-	-	-	-	-	-	-	-1.2	-	-	-	-	-	-
DF3	0.03	0.37	0.56	0.58	0.51	1.25	1.34	1.22	0.12	1.47	-	-	-	-
DF4	1.38	1.59	1.63	1.86	1.07	2.12	2.42	1.82	0.62	1.83	-	-	-	-

ICV=(Fe<sub>2</sub>O<sub>3</sub>(total)+K<sub>2</sub>O+Na<sub>2</sub>O+CaO+MgO+TiO<sub>2</sub>)/Al<sub>2</sub>O<sub>3</sub>.

CIA = [Al<sub>2</sub>O<sub>3</sub>/(Al<sub>2</sub>O<sub>3</sub> + CaO + Na<sub>2</sub>O + K<sub>2</sub>O)] × 100.

CIW = [Al<sub>2</sub>O<sub>3</sub>/(Al<sub>2</sub>O<sub>3</sub> + CaO + Na<sub>2</sub>O)] × 100.

DF1 = - 1.773 TiO<sub>2</sub> + 0.607 Al<sub>2</sub>O<sub>3</sub> + 0.76 Fe<sub>2</sub>O<sub>3</sub> (total) - 1.5 MgO + 0.616 CaO + 0.509 Na<sub>2</sub>O - 1.224 K<sub>2</sub>O - 9.09.

DF2 = 0.445 TiO<sub>2</sub> + 0.07 Al<sub>2</sub>O<sub>3</sub> - 0.25 Fe<sub>2</sub>O<sub>3</sub> (total) - 1.142 MgO + 0.438 CaO + 1.475 Na<sub>2</sub>O + 1.426 K<sub>2</sub>O - 6.861

DF3 = [30.638 TiO<sub>2</sub> - 12.541 Fe<sub>2</sub>O<sub>3</sub> (total) + 7.32 MgO + 12.031 Na<sub>2</sub>O + 35.402 K<sub>2</sub>O]/Al<sub>2</sub>O<sub>3</sub> - 6.382.

DF4 = [56.50 TiO<sub>2</sub> - 10.879 Fe<sub>2</sub>O<sub>3</sub> (total) + 30.875 MgO - 5.404Na<sub>2</sub>O + 11.112 K<sub>2</sub>O]/Al<sub>2</sub>O<sub>3</sub> - 3.89.

Table 3. Trace and rare earth element contents of the studied rocks. All in ppm.

Sample	3C	15B	16B	16E	17B	17G	26A	26C	26D	26J	Min	Max	Ave	PA
	Crd-	Crd-	Crd-	Crd-	Crd	Crd	And	And	And	And				
LFSE-LILE														
Rb	117	120.	135	132.	105.	136.	156	148	147	149.	105.	156	134.	160
Sr	56.9	68.9	51.8	47.6	82.5	35	62.3	64.7	108.	68.9	35	108.	64.7	200
Cs	5.01	4.59	4.68	4.1	5.3	5.58	25.3	33.2	41.6	26.5	4.1	41.6	15.5	15
Ba	451	389	443	497	419	583	994	684	614	641	389	994	571.	650
TRANSITIONAL ELEMENTS														
V	118	115	113	117	84	115	116	121	99	118	84	121	111.	150
Cr	90	90	90	90	70	90	90	90	80	100	70	100	88	110
Co	15.9	14.5	15.4	17.2	13.6	11.6	15.8	12.3	12.2	14.3	11.6	17.2	14.2	23
Ni	45	50	42	46	40	34	44	41	32	56	32	56	43	55
Zn	53	46	47	42	42	50	164	157	179	180	42	180	96	85
HFSE														
Ti	456	474	450	456	384	474	516	504	432	516	384	516	466	600
Y	29.5	30.5	28.8	30.1	24.1	32.1	30.5	30.7	26.9	31.7	24.1	32.1	29.4	27
Zr	173	180	173	168	153	167	173	186	218	197	153	218	178.	210
Nb	13.2	14.2	13.7	13.7	11.4	13.7	14.7	13	11.3	13.7	11.3	14.7	13.2	19
Hf	5	5.3	5.1	5.1	4.6	4.8	4.7	5.3	6	5.2	4.6	6	5.11	5
Ta	1.1	1.2	1.2	1.2	0.9	1.2	1	0.9	0.9	1	0.9	1.2	1.06	1.28
Pb	6	0	0	0	7	0	24	31	43	37	0.0	43	13.5	20
Th	13.2	12.2	12.4	12.6	9.15	12.8	11.8	11.5	10.2	12.4	9.15	13.2	11.8	14.6
U	3.42	3.83	3.33	3.63	2.53	3.66	3.21	3.28	2.9	3.62	2.53	3.83	3.34	3.1
Th/U	3.87	3.2	3.74	3.47	3.62	3.5	3.69	3.52	3.53	3.43	3.2	3.87	3.56	4.7
REE														
La	37.8	39	36.3	40.6	22.8	47.3	39.3	38.2	35	41.4	22.8	47.3	37.7	38.2
Ce	73.9	77.3	71.6	79.8	49	95	78.1	77.7	70.6	83	49	95	75.6	79.6
Pr	9.48	9.57	8.87	10.0	6.19	11.4	9.67	9.6	8.22	10.2	6.19	11.4	9.33	8.83
Nd	36.6	36.6	34.3	38.4	24.7	43.8	36.4	36.3	31.5	39.2	24.7	43.8	35.7	33.9
Sm	7.22	7.31	6.84	7.19	5.51	8.18	7.17	6.88	6.4	7.7	5.51	8.18	7.04	5.55
Eu	1.35	1.51	1.4	1.51	1.13	1.67	1.5	1.46	1.26	1.5	1.13	1.67	1.43	1.08
Gd	7.08	7.35	6.76	7.4	5.68	7.84	6.68	6.48	5.59	7.07	5.59	7.84	6.79	4.66
Tb	1.04	1.07	1.01	1.07	0.82	1.11	0.99	0.97	0.85	1.04	0.82	1.11	1	0.77
Dy	5.68	5.86	5.43	5.91	4.6	6.1	5.36	5.39	4.71	5.6	4.6	6.1	5.46	4.68
Ho	1.11	1.13	1.1	1.18	0.93	1.22	1.08	1.12	0.92	1.14	0.92	1.22	1.09	0.99
Er	3.34	3.41	3.28	3.43	2.73	3.72	3.17	3.08	2.82	3.29	2.73	3.72	3.23	2.85
Tm	0.49	0.49	0.47	0.51	0.39	0.52	0.45	0.46	0.36	0.45	0.36	0.52	0.46	0.40
Yb	3.22	3.14	3.07	3.22	2.5	3.45	2.87	2.75	2.51	3.19	2.5	3.45	2.99	2.82
Lu	0.45	0.46	0.46	0.47	0.37	0.5	0.46	0.44	0.37	0.45	0.37	0.5	0.44	0.44
∑REE	188.	194.	180.	200.	127.	231.	193.	190.	171.	205.	127.	231.	188.	184.
Eu/Eu*	0.89	0.97	0.97	0.97	0.95	0.98	1.02	1.03	0.99	0.96	0.89	1.03	0.97	-
Gd <sub>N</sub> /Yb	1.33	1.42	1.33	1.39	1.37	1.38	1.41	1.43	1.35	1.34	1.33	1.43	1.38	-
La <sub>N</sub> /Sm	0.76	0.78	0.77	0.82	0.6	0.84	0.8	0.81	0.79	0.78	0.6	0.84	0.78	-
La <sub>N</sub> /Yb	0.87	0.92	0.87	0.93	0.67	1.01	1.01	1.03	1.03	0.96	0.67	1.03	0.93	-

$$Eu/Eu^* = 2 \times Eu_N / (Sm_N + Gd_N)$$

The average weight percentages of SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub><sup>T</sup>, K<sub>2</sub>O, and P<sub>2</sub>O<sub>5</sub> in the Garmichay metapelites is similar to those observed for the same oxides in the PAAS, while the Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and CaO contents are slightly lower and MgO and Na<sub>2</sub>O contents are slightly higher in the Garmichay samples. With the exception for K<sub>2</sub>O and Na<sub>2</sub>O and to some extent Al<sub>2</sub>O<sub>3</sub>, other major oxides do not show any significant variations in the studied samples. Al<sub>2</sub>O<sub>3</sub> appears to be positively correlated with K<sub>2</sub>O (Fig.

5a), while Na<sub>2</sub>O shows a clear negative correlation with K<sub>2</sub>O (Fig. 5b).

#### *Low Field Strength or Large Ion Lithophile Elements (LFSE or LILE)*

The average Rb, Sr, and Ba abundances in the Garmichay samples are considerably lower than those observed in the PAAS, but the Cs contents are similar (Table 3).

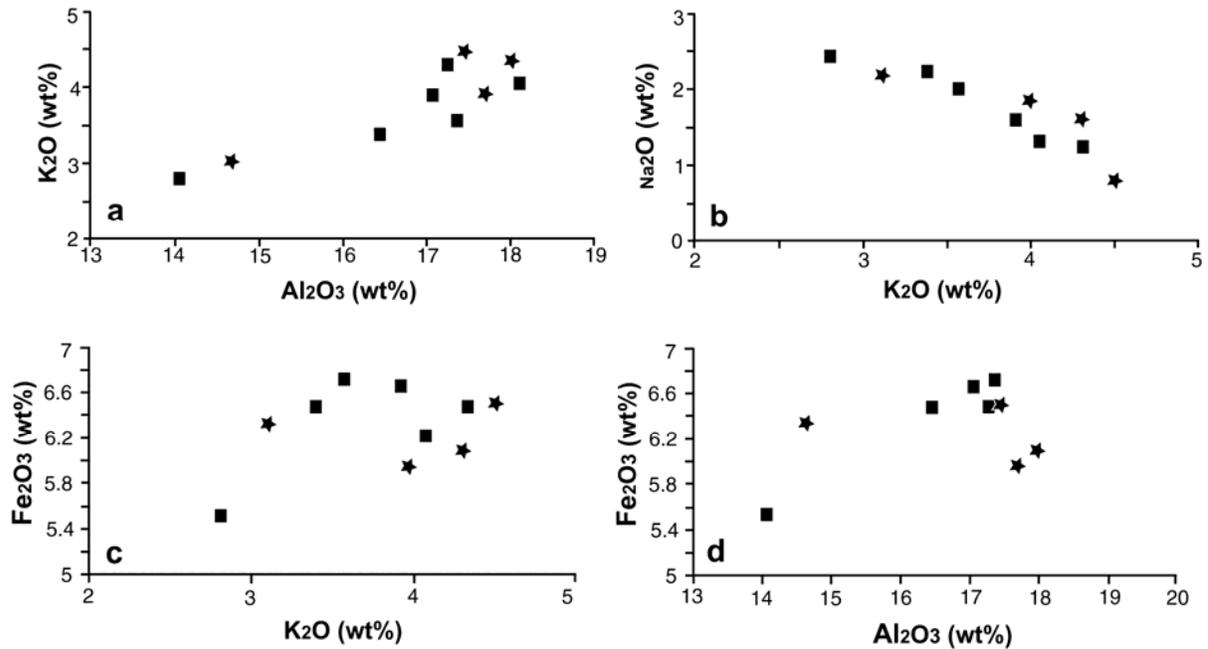


Figure 5. Variation diagrams for the major oxides.  $K_2O$  shows positive correlation with  $Al_2O_3$  and  $Fe_2O_3$ , while shows negative correlation with  $Na_2O$ . Stars show cordierite-free and squares show cordierite-bearing samples.

The range of variation of these elements in the studied samples is very wide, which may be due to the differing degrees of mobility of the elements during alteration of the protolith and/or differing conditions of metamorphism. As the  $K_2O$  content increases, Rb and Ba contents also increase, however, the Sr content decreases (Fig. 6). Cs does not show any significant trend.

Regarding the LFS elements, Ba enters the structure of the magmatic minerals during the magma crystallization phase in the intermediate igneous rocks, prior to the other elements of this group (Mason *et al.*, 1982). The high Ba content in the studied rocks may show that the source of the weathered materials, accumulated to form the protolith of the studied schists was of intermediate igneous rock origin.

This contention is supported by the observed low Cs contents of the studied samples. Cs tends to concentrate mainly in felsic and pegmatitic rocks of the final stages of magma fractionation with the probability of Ba concentrating in K-feldspar (Puchet, 1972). Since it is relatively resistant during alteration in comparison with biotite and plagioclase, K-feldspar is the main Ba carrier in argillaceous sediments (Heier and Billing, 1970). The Cs content in the argillite samples from rocks near Siahmansour village is almost five times greater than its concentration in argillite samples from east of the Garmichay River.

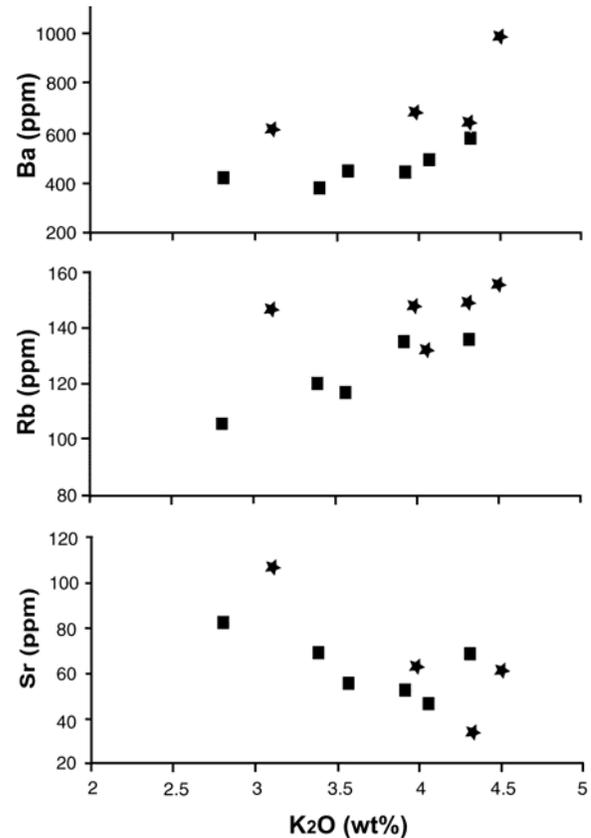


Figure 6. Positive correlation of  $K_2O$  with Ba and Rb and negative correlation with Sr.

### High Field Strength Elements (HFSE)

The HFSE contents in the Garmichay samples are similar to those present in the PAAS with the exception for Zr, which varies from 153 to 218 ppm (Table 3). This can be attributed to a different variation in modal percentage of zircon in different samples. Notably, there is a virtual lack of Pb in the samples from east of the Garmichay River, as compared to the PAAS. The narrow variation in samples within the Garmichay rocks may indicate that the sediments are derived from the same source.

Thorium and uranium behave differently during weathering. Under oxidizing conditions,  $U^{+4}$  transforms to  $U^{+6}$  during weathering which is more mobile. This results in an increase in the Th/U ratio in the protolith. For the metapelites from the Garmichay area, the Th/U ratio is in the range of 3.20 to 3.87, which is within the values obtained for the upper crust of 3.8 but is considerably lower than PAAS (McLennan and Taylor, 1980). This may reflect oxidizing conditions during the depositional process of the Garmichay argillaceous rocks.

### Transition Elements

The average of transition elements in the Garmichay samples is slightly lower than that observed in the PAAS, with the exception for Zn (Table 3). The Zn content in the metapelites from the Siahmansour area is 3 to 4 times higher than its concentration in samples from the east of the Garmichay River (Table 3).

### Rare Earth Elements (REE)

The REE abundances in the Garmichay metapelites are very similar to those obtained for the PAAS (Table 3). The variation of abundances for these elements falls in a very narrow range, with the exception for La, Ce, and Nd, which show broader ranges of 22.8 to 47.3, 49-95, and 24.7 to 43.8 ppm, respectively. The LREE show a larger variation than the MREE and the HREE (Fig. 7).

The metapelites exhibit a considerable depletion in the LREE ( $La_N/Sm_N=0.60-0.84$ ) and a slight depletion in HREE ( $Gd_N/Yb_N=1.33-1.43$ ) in comparison to the PAAS (Fig. 7). The ratio of  $Eu/Eu^*=0.89-1.03$ , giving an average of 0.97, indicates no significant Eu anomaly in the metapelites. The average of the  $\Sigma REE$  is similar to that of the PAAS but the range is higher ( $\Sigma REE=127.35-231.89$ ).

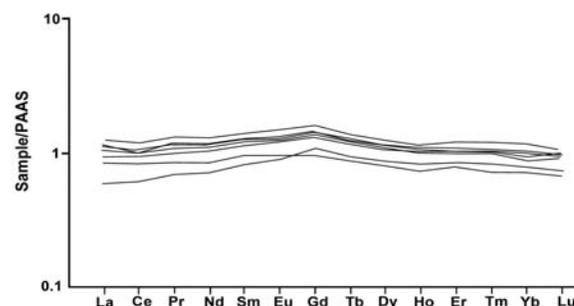


Figure 7. Almost flat REE pattern for the studied rocks normalised to PAAS

### The Nature of the Original Sediments

In order to characterize the lithological features of the original sediments, sample data plots are shown on the discrimination diagram (Fig. 8) of  $\log (Fe_2O_3/K_2O)$  vs.  $\log (SiO_2/Al_2O_3)$  after Herron (1988). This shows a distinct cluster of data plots predominantly in the shale field, with two samples plotting on the line, separating the shale and wacke fields (Fig. 8). Source materials for the original clay-rich rocks may be either of igneous rock origin or recycled from sedimentary rock. Data plotted on the  $P_2O_5/TiO_2$  versus  $MgO/CaO$  discrimination diagram after Werner (1987) indicate reworked sedimentary origin for the rocks (Fig. 9).

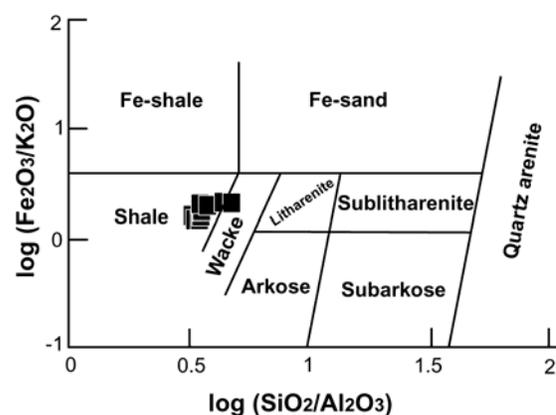


Figure 8. The studied metapelites had shale to wacke protolith

Furthermore, it suggests that the lithology of the protolith was of a recycled quartz sedimentary type (Roser and Korsch, 1988) (Fig. 10A and B). DF1, DF2, DF3, and DF4 are discrimination factors which are explained in the footnotes of Table 2. Although there are no certain criteria for determining the nature of the parental igneous rocks of the recycled sediments, Pinto *et al.* (2004) have shown that it is possible to use some diagrams for this purpose.

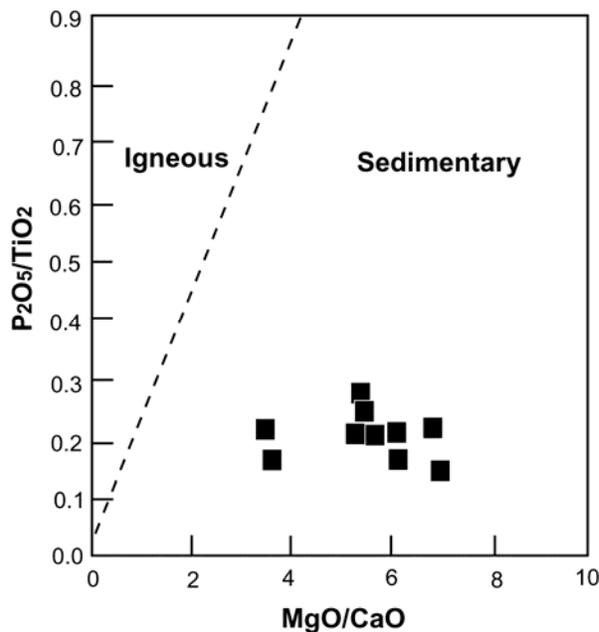


Figure 9.  $P_2O_5/TiO_2$  versus  $MgO/CaO$  diagram which shows a sedimentary rock as the protolith for the studied metapelites

Elements with minimum mobility during sedimentary processes are used to discriminate between various igneous source rocks. Figure 11 indicates that andesite was the initial parent rock for the metapelites forming sediments. This is compatible with the LFSE results. The discrimination diagram of Chemical Index of Alteration (CIA) (Nesbitt and Young, 1982) versus Index of Compositional Variability (ICV) (Cox *et al.*, 1995; Potter *et al.*, 2005) also shows the recycled quartz metasediments, as the protolith of the metapelites were themselves originated from an andesitic source (Fig. 12).

### Weathering and Depositional Cycle Prior to Metamorphism

In order to evaluate the alteration due to weathering of the source materials of the Garmichay metapelites before metamorphism quantitatively and qualitatively, two indices called the chemical index of alteration (CIA) and CIW (Chemical Index of Weathering, Harnois, 1988) are used. The formula and results of calculation of these two indices is provided in the footnotes of Table 2.

The CIA is conventionally used in the calculation of alteration. Values of 90-100 indicate an intense alteration of most, or all, of the feldspar minerals into resistant clays such as kaolinite and gibbsite (Nesbitt and Young, 1982).

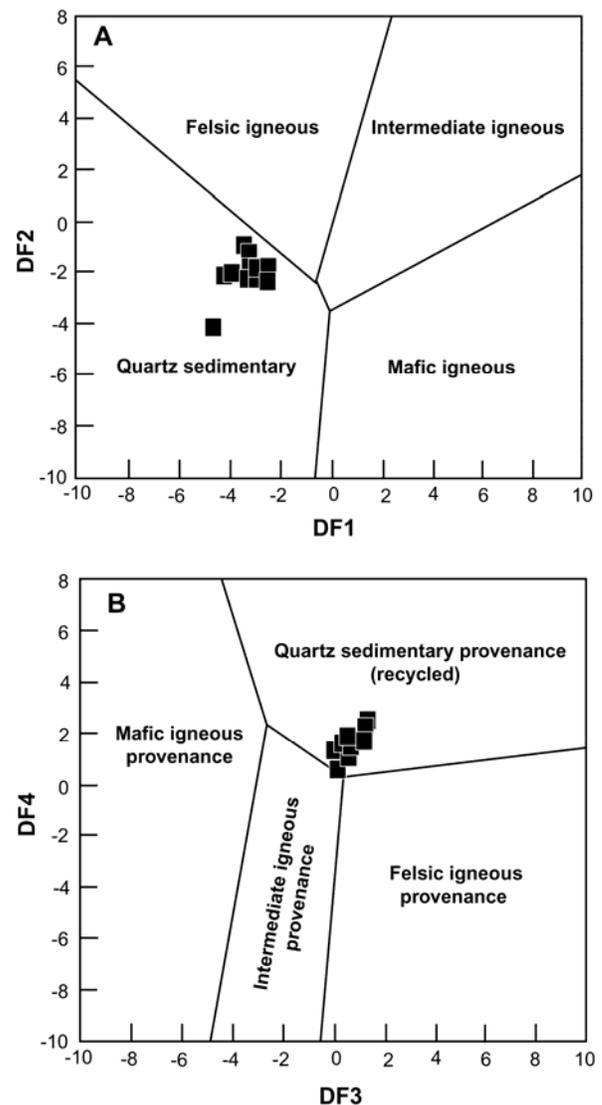


Figure 10. The original sedimentary rocks forming the Garmichay metapelites were of recycled quartz sedimentary type.

In addition, high values of CIA indicate a relative loss of  $K^+$ ,  $Na^+$ , and  $Ca^{2+}$  compared to that of  $Al^{3+}$  and  $Ti^{4+}$  during alteration process. The CIA values for Phanerozoic shales are generally between 70-75, which indicates moderate degrees of weathering in source rock areas, with the formation of muscovite, illite, and smectite.

The CIA values for the Garmichay metapelites are between 63-71; a range slightly lower than the range for the Phanerozoic shales but comparable well to PAAS (69). This result shows that protolith of the Garmichay metapelites experienced low to moderate alteration condition before metamorphism (Fig. 13).

It should be noted that the application of the CIA to sediments, which may be subject to a late K enrichment during diagenesis, will produce spurious CIA values, (Fedo *et al.*, 1995).

As an alternative index which does not include potassium, Harnois (1988) proposed the use of the Chemical Index of Weathering (CIW) [ $Al_2O_3 / (Al_2O_3 + Na_2O + CaO) \times 100$ ] (Table 2).

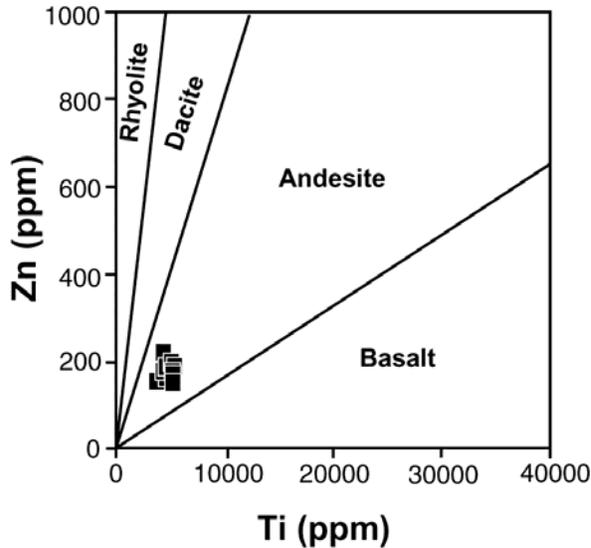


Figure 11. Diagram of Pinto *et al.* (2004) indicating andesite as the parental igneous rocks for the sediments as protolith of the studied metapelites.

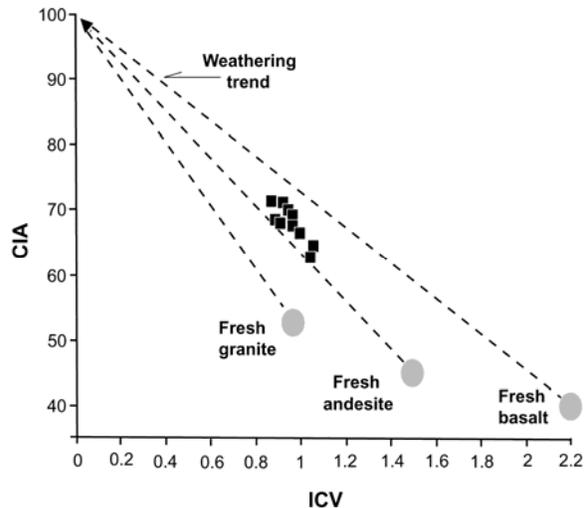


Figure 12. CIA versus ICV diagram of Potter *et al.* (2005) showing that the studied metasediments plot along the andesite weathering trend.

Most post-Archaean shales have a CIW in the range 80-95, whilst the range for the Archaean shales is 90-98 (Condie, 1993).

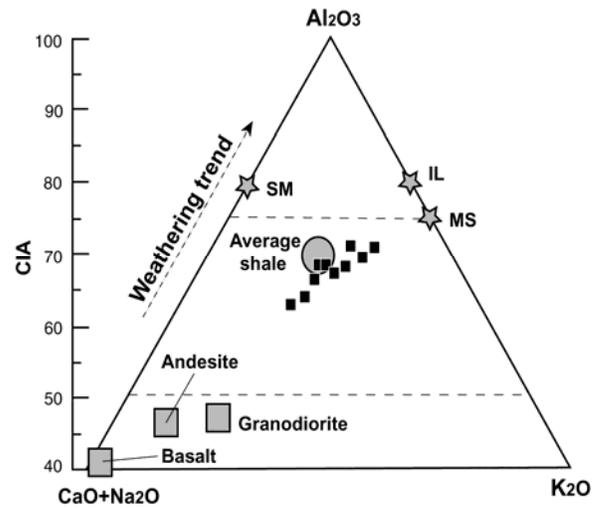


Figure 13. Similar CIA for the Garmichay metapelites to that of PAAS indicating that protolith of the Garmichay metapelites experienced low to moderate alteration.

The CIW values for the Garmichay metapelites lie in the range of 73-88.6 (average of 81.6) which overlaps, in part, the range of the post-Archaean shales and shows no match with the Archaean shales.

Both the CIA and CIW reflect the feldspar to clay ratio in the rocks with the nature of the source rock having no influence on these indices. In order to indicate the influence of the source rock, Cox *et al.* (1995) added  $Fe_2O_3^T$  and MgO and introduced the Index of Compositional Variability (ICV). High ICV values (higher than that for PAAS, 0.85) indicate immature sediment, rich in non-clay minerals, deposited at an active continental margin (Long *et al.*, 2008). Low ICV values indicate alteration of feldspars to Al-rich clay minerals. The high ICV value (higher than that for PASS, 0.85) indicates an immature sediment deposited at an active continental margin (Long *et al.*, 2008).

The data point cluster on the  $Na_2O/K_2O$  versus  $SiO_2$  diagram strongly suggests an active continental margin depositional environment for the protolith of the Garmichay metapelites (Fig. 14). The ICV range for the Garmichay metapelites is 0.87 to 1.05 (Table 2), which is higher than the PAAS (0.85) value. This suggests that the metapelites originally formed as immature sediments, likely to have been deposited in an active continental margin (ACM) tectonic setting. As stated previously, the Th/U ratio for the studied rocks is similar to the ratio obtained for the upper crust (Rudnick & Gao, 2003). Variation of  $Gd_N/Yb_N$  and  $La_N/Sm_N$  versus CIA (Zhang *et al.*,

1998) indicates that the trend is almost linear and depletion or enrichment of LREEs and HREEs is independent of the degree of alteration of the sediments (Fig. 15).

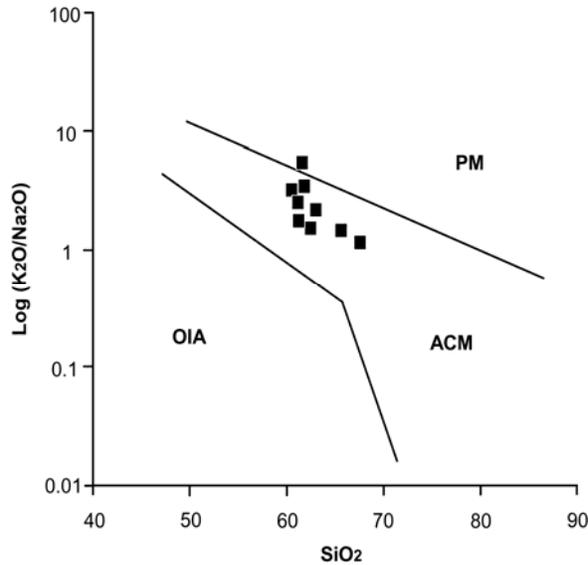


Figure 14. Protolith sediments of the Garmichay metapelites more likely deposited in an active continental margin tectonic setting.

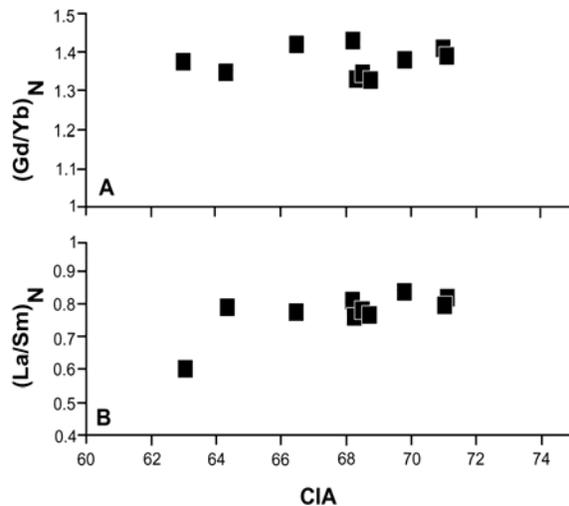


Figure 15.  $Gd_N/Yb_N$  and  $La_N/Sm_N$  versus CIA linear trends, which indicates that depletion or enrichment of LREEs and HREEs is independent of degree of alteration of the sediments.

### Post-Deposition Alteration Effects

Silicification and K metasomatism are two important processes that can affect sediments after deposition (Cullers *et al.*, 1993; Fedo *et al.*, 1995). Silicification may occur due to hydrothermal

metasomatism or interaction of the sediment with sea water during sedimentation or a combination of both (Van Kranendonk, 2006). Due to these processes, major elements such as Ca, Mg, Na, and Fe leach out from the sediments, while Si and K concentrate (Cullers *et al.*, 1993). The  $SiO_2/Al_2O_3$  ratios of the Garmichay metapelites (3.34-4.80) may indicate limited Si addition to the rocks after sedimentation.

### P-T and Chemistry Control on Metamorphic Mineral Assemblages

#### P-T Conditions of Metamorphism

Differences in metamorphic mineral assemblages in the Garmichay metapelites can be attributed to difference in P-T of metamorphism, differences in whole rock chemistry, or a combination of both. Original cordierite is highly altered in the studied metapelites of the Garmichay area. It was not possible to obtain suitable mineral chemical data in order to perform conventional pressure-temperature calculations, based on mineral compositions on these rocks. As an alternative, a whole rock chemistry and pseudosection approach was used to calculate the pressure and temperature conditions of metamorphism for representative samples.

THERIAK-DOMINO software (deCapitani & Brown, 1987, database of Berman 1988) was used for pseudosection calculations, which were carried out on three samples. Total iron was considered to be  $Fe^{2+}$  and pseudosections were projected from plagioclase, magnetite, and ilmenite as excess phases. Sample 17b contains solely ex-cordierite porphyroblasts (pinite), sample 3c contains both pinite and fresh andalusite porphyroblasts, and sample 26d contains only fresh andalusite porphyroblasts. Other minerals present in these rocks include:  $Bt+Ms+Qz\pm Chl$  and non-KFMASH minerals (mainly oxide minerals and plagioclase). Figure 16 shows pseudosections calculated for these samples.

The pressure calculated for sample 17b ( $Bt+Ms+Chl+Crd$ , Fig. 16A) is slightly higher than 1kbar with temperature  $\sim 500^\circ C$ . The temperature calculated for sample 3c ( $Bt+Ms+Crd+And$ , Fig. 16B) is slightly higher than  $500^\circ C$  and for sample 26d ( $Bt+Ms+And$ ) pressure (up to 2.5 kbar) and temperature (up to  $600^\circ C$ ) are both higher than those for the other two samples.

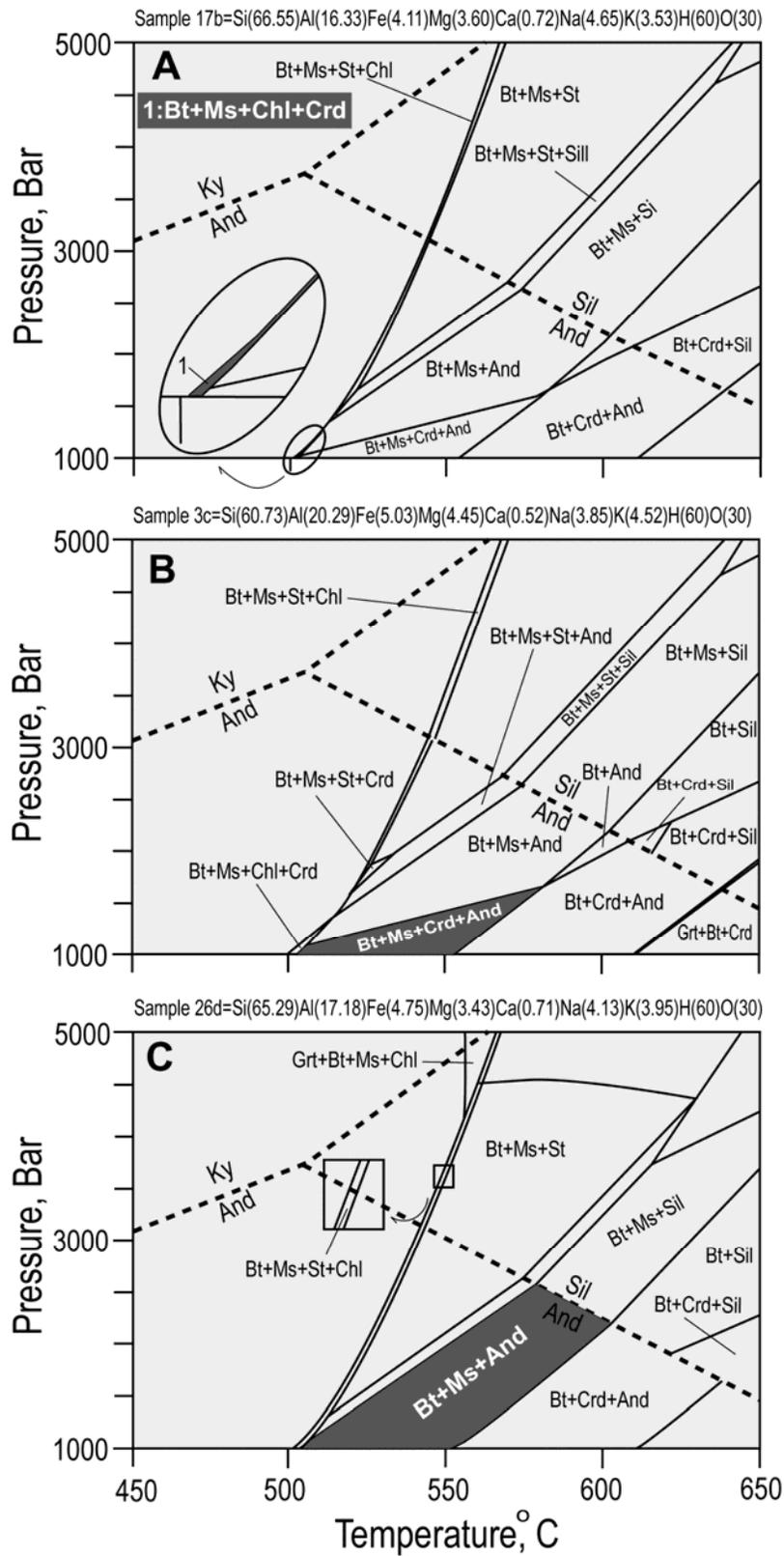


Figure 16. Pseudosections calculated for three representative samples. Parageneses found in each samples, are shown with dark grey field.

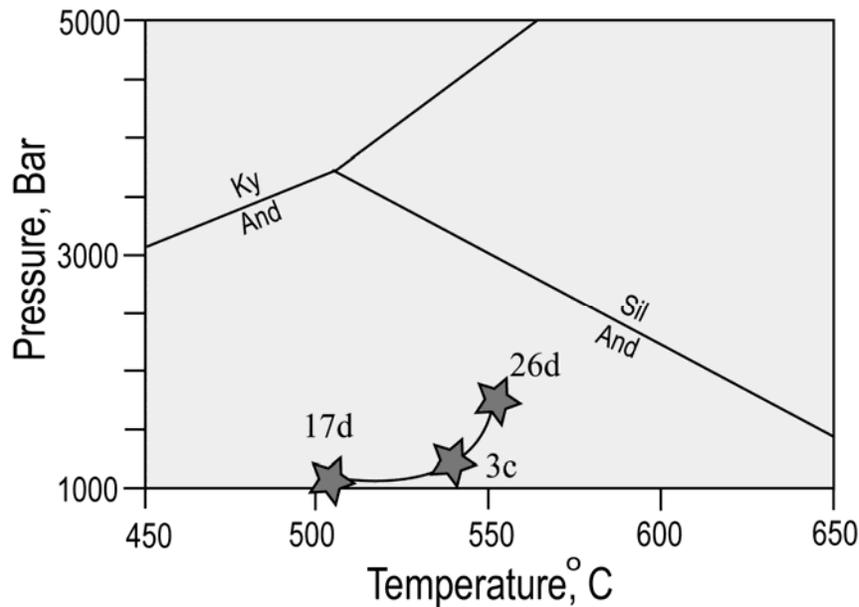


Figure 17. Pressure and temperature of metamorphism of the representative samples. All samples plot within the andalusite stability field. There are small differences in pressure and temperature of metamorphism.

Figure 17 shows P-T estimates for all three samples. In general, it may be assumed that the observed differences in temperature and pressure conditions, are the factors controlling the metamorphic mineral assemblages.

There are, however, uncertainties in these estimations with P-T differences falling in a narrow range for rocks with different mineral assemblages. Therefore, perhaps, the whole rock chemistry of the original pelites played a more significant role in determining the final metamorphic mineral assemblages.

#### Whole Rock Chemistry Control on Metamorphic Mineral Assemblages

Mineralogically, the metapelites of the Garmichay area can be divided into three main groups; 1. Ex-cordierite (pinnite) and andalusite-bearing, 2. Those containing only ex-cordierite porphyroblasts, and 3. Porphyroblastic andalusite-bearing samples. The main whole rock control on the crystallization of cordierite in pelitic rocks is the  $\text{Fe}^{2+}/\text{Mg}$  ratio of the protolith (Bucher and Grapes, 2011), with cordierite forming in the more Mg-rich pelites. Figure 18 shows that there is no difference in the  $\text{Fe}^{2+}/\text{Mg}$  ratio for samples with different mineral assemblages, suggesting that these major oxides abundance were not a controlling factor in the resulting mineral assemblages.

The presence of some minor oxides has been

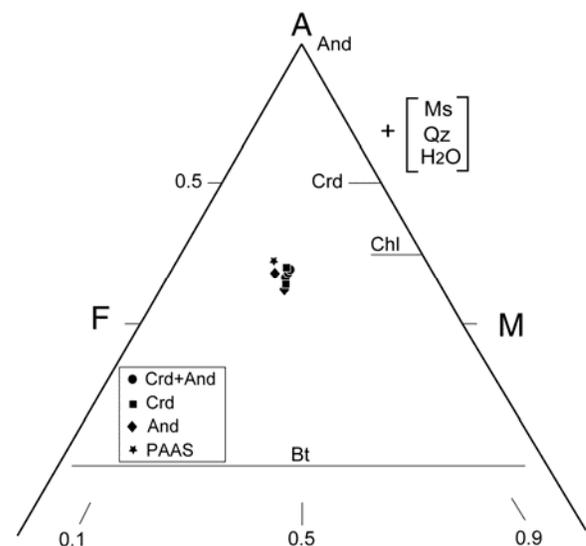


Figure 18. AFM diagram projected for samples with different mineral assemblages. The projection is made from excess quartz, muscovite and water. PAAS composition is plotted for comparison. As it can be seen, the Fe and Mg content of the samples are very similar.

shown to significantly affect the resulting mineral assemblages in metapelitic rocks. For instance, Mahar *et al.* (1997) showed that the presence of low abundances of MnO can cause a reduction by about 100°C in the appearance of the garnet isograd. According to their petrogenetic grid, cordierite and andalusite co-exist at a temperature of ~525°C at a pressure of 3kbar in the MnO-K<sub>2</sub>O-FeO-MgO-

$\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{H}_2\text{O}$  (MnKFMASH) system. In the KFMASH system, cordierite and andalusite co-exist at a temperature of  $\sim 540^\circ\text{C}$  and pressure of  $\sim 4.2$  kbar.

Wei *et al.* (2004) also showed that the addition of Mn to the KFMASH system increases the stability field of garnet and to a lesser extent, the stability fields of the aluminosilicates. The addition of MnO also causes decrease in the stability fields of staurolite and cordierite and, to a lesser extent, that of chlorite. In addition to the effects of the MnO abundances on the mineral assemblages of metapelites, Droop and Harte (1995) showed that addition of Zn to the KFMASH system reduces the temperature, at which, staurolite is formed in metapelites.

Nichols *et al.* (1992) studied the effect of Zn on phase equilibria among spinel-garnet-cordierite paragenesis and concluded that the addition of Zn to the system increases the stability fields of garnet-hydrous cordierite and spinel-hydrous cordierite. There are no garnets present in the Garmichay metapelites and MnO abundances are relatively low (0.03 to 0.06 wt%). Wei *et al.* (2004) showed that the effect of MnO on mineral assemblage should be considered together with the presence of  $\text{Al}_2\text{O}_3$  and  $\text{K}_2\text{O}$  in the metapelites. Figure 19 shows that samples containing cordierite and those without cordierite exhibit differences in their MnO contents.

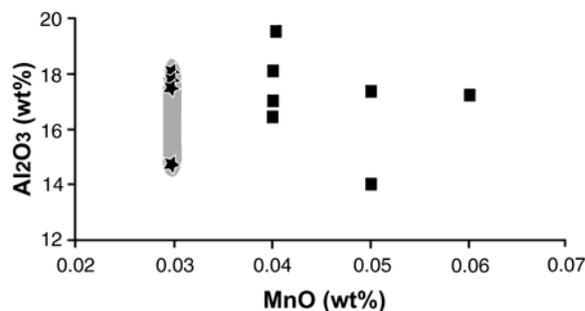


Figure 19. Although the variation in MnO content is very narrow, but cordierite-bearing samples show higher MnO content on  $\text{Al}_2\text{O}_3$  versus MnO diagram.

There are no significant differences in  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{K}_2\text{O}$  abundances (Fig. 5). Therefore, MnO could have significant effect on mineral assemblages.

According to Figure 20, samples lacking pinite (ex-cordierite) contain considerable amounts of Zn while samples containing pinite (ex-cordierite) have much lower Zn contents. This is apparently in conflict with observations by Nichols *et al.* (1992).

According to their studies, Zn increases the stability field of cordierite. This apparent discrepancy can be attributed to severe alteration of cordierite and formation of pinite in our samples, in which Zn is leached out from the rocks. It should be mentioned that Nichols *et al.* (1992) studied Zn effect on cordierite stability in the system cordierite-spinel-garnet. There is no garnet and spinel in our rocks and this apparent discrepancy could be partly due to absence of these minerals.

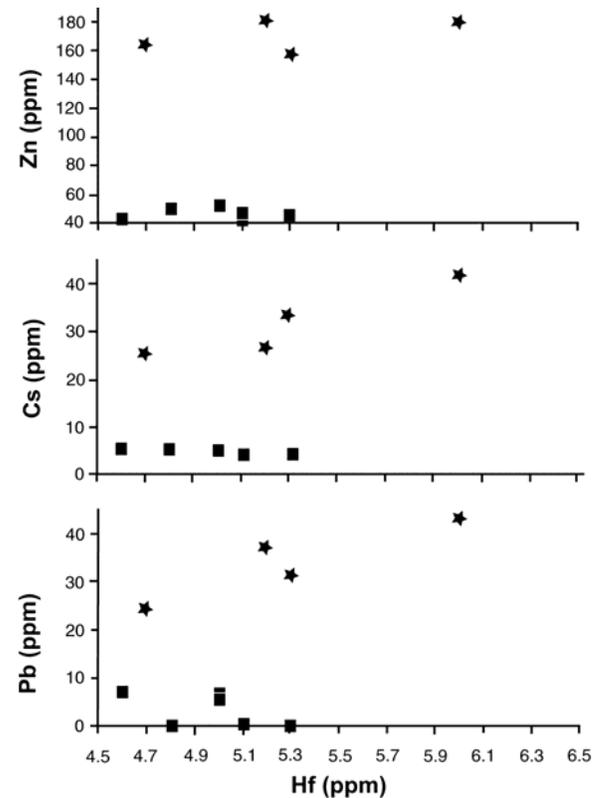


Figure 20. There is a distinct difference in Pb, Cs and Zn content of cordierite-bearing samples (squares) and cordierite-absent (stars) samples.

Between MnO and Zn, MnO had meager control (if any) on mineral assemblages of the Garmichay metapelites, since its concentration varies from 0.01 to 0.03 wt% which is a very narrow variation. More likely, Zn had the major role in controlling the mineral assemblages in these rocks. Cs, Zn, and Pb contents in samples lacking pinite (ex-cordierite) are several times higher than concentration of these elements in pinite-bearing samples.

Hf shows similar concentration in all sample types. Therefore, binary diagrams of Hf versus Cs and Hf versus Pb are constructed to study the possible effects of these elements on the mineral

assemblages of the studied samples. According to Figure 20, samples lacking pinite have higher contents of Cs and Pb. Again, this is at odds with observations on the chemistry of natural cordierites.

Bertoldi *et al.* (2004) showed that cordierite can take 0.1 up to 41 ppm of Cs. It is not easy to say anything about Pb. Cs probably accumulated in the structure of cordierite during crystallization of this mineral, but later, due to extensive alteration of cordierite, this element was almost completely leached out from ex-cordierite-bearing samples, while there are detectable amounts of this element in samples lacking ex-cordierite. Probably the behavior of Cs is similar to that of Zn in the Garmichay metapelites.

### Conclusion

Metapelitic rocks in the Garmichay area in NW Iran are older than Cretaceous but their exact age is unknown. The main minerals in the studied samples are muscovite, chlorite, biotite, quartz, pinitized cordierite (pinite or ex-cordierite), andalusite, plagioclase, and oxide minerals. These rocks can be divided into four main groups, based on metamorphic porphyroblasts. They are pinite-bearing, andalusite-bearing, pinite and andalusite-bearing rocks, and rocks lacking pinite and andalusite.

Investigations on the Garmichay metapelites indicate that their sedimentary protolith was clay-

rich rocks of a reworked nature, most likely from an original andesite to andesite-basalt source. The source materials experienced low to moderate chemical alteration. The resulted sediments deposited in an active continental margin tectonic setting. They also experienced limited Si addition after sedimentation.

Pressure-temperature conditions at the peak of metamorphism were ~1-2.5 kbar and 500-600°C, corresponding to low-pressure-medium-temperature metamorphic gradient.

Whole rock chemistry shows that there is not much difference in major oxide contents of the studied samples with different metamorphic mineral assemblages. However, some minor elements show meaningful differences between pinite-bearing and pinite-free samples. Zn content is more pronounced in this regard. It can be deduced that minor elements had important role in controlling mineral assemblages in the Garmichay metapelites, more important than pressure and temperature controls.

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