

Lithos 51 (2000) 181-203



www.elsevier.nl/locate/lithos

The geochemistry of shales, siltstones and sandstones of Pennsylvanian-Permian age, Colorado, USA: implications for provenance and metamorphic studies

Robert L. Cullers *

Department of Geology, Kansas State University, 108 Thompson Hall, Manhattan, KS 66506-3201, USA Received 27 October 1998; accepted 12 October 1999

Abstract

A series of shales and sandstones found near the source of the Sangre de Cristo, Belden, and Maroon Formations from central Colorado were examined petrographically and were analyzed for major and selected trace elements, including the REE. The sandstones from the Belden Formation have higher quartz/feldspar ratios than do those from the Maroon and Sangre de Cristo Formations, Also, the alkali feldspar (i.e., orthoclase, microcline, perthite)/plagioclase ratio decreases in the order Sangre de Cristo Formation > Maroon Formation > Belden Formation, but the CIW' (chemical index of weathering = molecular $[Al_2O_3/(Al_2O_3 + Na_2O)]*100$) decreases in the order Belden Formation > Sangre de Cristo Formation > Maroon Formation. This suggests that the Belden Formation had a more plagioclase-rich granitoid source and more intense weathering of the source than did the Maroon and Sangre de Cristo Formations. Also, the variation in the elemental composition within the terrigenous sediment may be explained in terms of the variation in the observed minerals. Elemental ratios critical of provenance are statistically the same between the finer sediment of the Maroon and Sangre de Cristo Formations and fall within the range of a granitoid provenance, suggesting a similar granitoid source composition for the two formations. The fine sediment from the Belden Formation, however, has significantly more negative Eu anomalies and lower La/Sc and Th/Cr ratios than those of the Maroon and Sangre de Cristo Formations, suggesting a more differentiated granitoid source for the Belden than for the Maroon and Sangre de Cristo Formations. Most elemental concentrations or ratios vary by a factor of 0.12 to 60 between adjacent fine and coarse sediment (< 1-m distances). Thus, it is not recommended that metasedimentary sequences similar in composition to this study be examined to determine element mobility during metamorphism as the variation due to sedimentary processes is so large. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Shales; Sandstones; Provenance; Trace elements; Rare-earth elements; Metamorphism

1. Introduction

There have been a variety of studies of the elemental composition of shales and sandstones or recent soils and sediment with the goal of determining

0024-4937/00/\$ - see front matter © 2000 Elsevier Science B.V. All rights reserved. PII: S0024-4937(99)00063-8

the provenance of sedimentary rocks (Nesbitt, 1979; Maughin, 1980; Cullers, 1988, 1994b; Cullers et al., 1987, 1988; McLennan et al., 1990, 1993; Wronkiewicz and Condie, 1990; Murray et al., 1991; Gouveia et al., 1993; Condie et al., 1995; Cox et al., 1995; Girty et al., 1996). The provenance of sand-

^{*} Fax: +1-913-532-7004; e-mail: rcullers@ksuvm.ksu.edu

stones has traditionally been determined by classic petrographic techniques, but in some cases, sandstones with a significant fine fraction may have trace element ratios that may give added information about the provenance (Cullers and Stone, 1991; Cullers and Berendsen, 1998). The use of trace element and isotopic ratios in shales not associated with much sandstone, however, has provided the only information about the provenance of sedimentary rocks (Mc-Lennan et al., 1983; Condie, 1991; Condie and Wronkiewicz, 1990; Fyffe and Pickerill, 1993; Girty et al., 1993; Cullers, 1994b; Ugidos et al., 1997). For example. La and Th are more concentrated in silicic than basic igneous rocks, whereas, Co. Sc. and Cr are more concentrated in basic than silicic igneous rocks. In addition, these elements are relatively immobile during weathering (Cullers et al., 1987; Condie and Wronkiewicz, 1990; Cullers, 1994a; Cullers, 1994b). Thus, ratios of La or Th to Co. Sc. or Cr are sensitive indicators of source rock compositions. Also silicic igneous rocks contain negative Eu anomalies (Eu/Eu* from chondrite-normalized plots of the REE) and basic igneous rocks contain little or no Eu anomalies, and the size of the negative anomalies in the provenance appear to be preserved in fine-grained sediment (Cullers, 1994b; Cullers et al., 1987).

There have been few detailed studies, however, of sequences of interbedded shales and sandstones to determine the chemical variability within such sequences. Most studies have (Moss et al., 1995a) sampled only a few "representative samples" sometimes over large distances to make comparisons. As a consequence, we do not understand very well how local variability of the composition of shales and sandstones compare to regional variation in their composition. Such studies would help to assess how much variation in shale and sandstone composition may be due to sedimentary processes and how much is due to variation in provenance. A better understanding of how sedimentary processes and composition of the provenance affect the composition of sandstones and shales could also help to understand how much of the variation in the chemical composition in metamorphosed sedimentary rocks could be due to metamorphic processes as opposed to sedimentary processes and/or source composition (Moss et al., 1995b).

In this study, associated samples of shales and sandstones formed near the source have been taken with the goal of comparing compositional similarities and differences in elemental composition of sediment of different grain sizes (shales-siltstones, siltstones-fine sandstones, and medium-coarse sandstones) deposited in close proximity to each other. First, the composition of elemental ratios can be compared in the different size fractions to determine whether or not they are giving the same information about the provenance. Second, the results of this study should be especially important in basins that have been extensively metamorphosed (Moss et al., 1996). In such basins, knowledge of the potential variations in composition due to changing provenance or sedimentary processes may aid in the determination of elemental mobility due to metamorphic processes.

2. Geology

The units studied in this paper are the Belden, Maroon, and Sangre de Cristo formations, and they are located in Colorado, USA (Fig. 1). The Belden

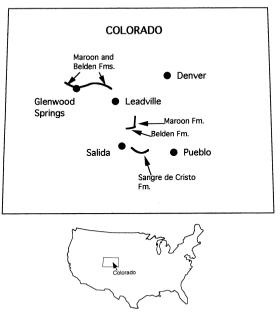


Fig. 1. Index map of Colorado with selected urban centers for reference. Samples were obtained along the solid, curved lines in the map. The map of the USA shows the location of Colorado.

Formation is Lower to Middle Pennsylvanian in age and the Maroon and Sangre de Cristo Formations are Upper Pennsylvanian to Lower Permian in age (Fig. 2). Sediment in these formations was derived from the adjacent uplifts, and was deposited in the north—south trending Colorado trough (De Voto, 1980; Lindsey et al., 1987).

The Belden Formation consists mostly of dark gray to black shale. It also contains minor feldspathic sandstones and limestones (Brill, 1952; Tweto and Lovering, 1977; De Voto, 1980; Nuccio and Schenk, 1987). Sediment in the Belden Formation was deposited in a shallow marine or deltaic environment (Johnson, 1987). The climate during deposition was probably humid (Lindsey et al., 1987). Samples of shale and feldspathic sandstone were collected from Glenwood Springs to near Buena Vista, Colorado (west to east, respectively, in Fig. 1).

The Maroon Formation consists of up to 4600 m of fine to coarse arkosic sandstones, conglomerates, siltstones, and shales (De Voto, 1972, 1980; Johnson, 1987). However, extreme variation in thickness near uplifted fault blocks has been documented, and sediment coarsens adjacent to uplifted fault blocks (De Voto, 1972). Sediment in the Maroon Formation was deposited in arid conditions in alluvial environ-

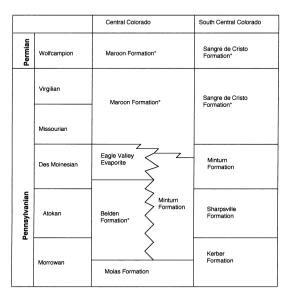


Fig. 2. Pennsylvanian and Lower Permian stratigraphy in central and south-central Colorado. Units marked with an * are those analyzed in this study (De Voto, 1980; Maughin, 1980).

ments that include alluvial fans, braided streams, basin center low energy streams, and flood plains (De Voto, 1980; Johnson, 1987). Samples of the Maroon Formation were collected over the same region as those for the Belden Formation (Fig. 1).

The Sangre de Cristo Formation ranges up to 2000 m in thickness and consists of lithologies similar to those observed in the Maroon Formation. In addition, both formations were deposited under similar climatic conditions and in similar depositional environments (Bolyard, 1959; De Voto, 1980; Lindsev et al., 1987). In addition to arkosic sandstones, conglomerates, siltstones, and shales, the Sangre de Cristo Formation also locally contains limestone. gypsum, and coal. In some places, the Sangre de Cristo Formation includes an upper member (Crestone Conglomerate) composed of coarse arkosic sandstone and boulder conglomerates interpreted as debris flows, mud flows, and stream flow-sheet flow deposits (Flores, 1984; Lindsey et al., 1987). Samples of the Sangre de Cristo Formation were collected in the section along the Arkansas River east of Salida, Colorado, hence, samples of the Crestone Conglomerate were not collected (Fig. 1).

3. Samples and analytical procedures

A portion of the relatively unweathered samples was gently broken into pebble size or smaller fragments in a steel mortar and pestle, and then was ground to a small enough size to allow passage through a 120-mesh sieve in an agate vial using a Spex mixer-mill. Thin sections stained to distinguish alkali feldspar (orthoclase, microcline, or perthite) from plagioclase were made from a portion of the unground sample. Point counts (about 500 points) were done on each thin section to estimate modal mineralogy.

Atomic absorption was used to analyze about 0.2 g of the ground samples for the major elements, Rb, and Sr (Medlin et al., 1969; Shapiro, 1978). Neutron activation was used to analyze about 0.5 g of the ground samples for La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Na, Fe, Rb, Ba, Th, Hf, Sc, Cr, and Cs (Gordon et al., 1968; Jacobs et al., 1977). Elements analyzed by both methods agreed well and were averaged. Re-

Table 1
The petrography of selected sandstones

	Sangre de	Cristo Fo	ormation												
	SDC-4	SDC-5	SDC-6	SDC-7	SDC-8	SDC-12	SDC-13	SDC-18	SDC-19	SDC-21	SDC-22	SDC-24	SDC-25	SDC-26	SDC-28
	coarse silt	t medium	medium	siltstone	siltstone	siltstone	medium	fine to	very fine	fine to	medium to	siltstone	medium to	siltstone	fine ss
	very fine	to coarse	to coarse	to fine	to fine	to fine	to coarse	medium	to fine	coarse	coarse	to fine	coarse	to fine	
	ss-1	SS	SS	SS	SS	SS	SS	SS	SS	SS	SS	SS	SS	SS	
Quartz															
Monocrystalline- nonundulatory	19.6	17.3	23.7	23.1	18.2	21.8	21.0	31.8	25.0	23.8	19.3	17.9	15.3	24.5	17.0
Monocrystalline- undulatory	9.2	8.2	4.0	4.6	4.1	3.0	0.6	2.0	0.4	1.9	1.4	3.4	10.9	1.7	0.6
Polycrystalline	0	0.6	1.2	0.5	0	0	0.6	0	1.3	0.5	0	0	8.7	1.2	0
Total quartz	28.8	26.1	28.9	28.2	22.3	24.8	22.2	33.8	26.7	26.2	20.7	21.3	34.9	27.4	17.6
Feldspar															
Plagioclase	16.5	26.1	28.9	27.3	19.4	19.8	23.3	16.2	25.9	31.0	20.2	21.8	26.2	26.6	17.6
Alkali feldspar	42.7	28.9	30.5	28.7	34.7	25.7	11.9	16.9	26.8	31.9	17.5	12.9	34.5	24.9	23.6
Total feldspar	59.2	55	59.4	56.0	54.1	45.5	35.2	33.1	52.7	62.9	37.7	34.7	60.7	51.5	41.2
Rock fragments	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Other minerals															
Muscovite	0.4	trace	1.2	0.5	0.6	0	0	0.7	0	trace	trace	trace	0	0.4	1.2
Biotite or chlorite	0.8	0.3	0.4	1.9	0	trace	0	0	1.3	0	0	0.6	0.4	0.8	1.8
Opaques	0.4	2.2	0.8	trace	0.6	0.5	0.6	trace	0.9	trace	0	0	1.3	0	0
Miscellaneous	0	0	0	0	0	trace	0	trace	trace	trace	0	trace	0	trace	trace
Total of other minerals	1.6	2.5	2.4	2.4	1.2	0.5	0.6	0.7	2.2	0	0	0.6	1.7	1.2	3
Matrix															
Hematitic clay	0	5.0	3.2	13.4	20.0	17.8	31.8	0.6	0.4	1.4	17.5	33.5	0.4	11.6	23.0
Clay	0.8	0.7	0.4	0	2.4	5.9	0	0	1.8	0.5	0	0.6	0.4	0	1.9
Total clay	0.8	5.7	3.6	13.4	22.4	23.7	31.8	0.6	2.2	1.9	17.5	34.1	0.8	11.6	24.9
Cement															
Quartz	0.4	0	1.7	trace	0	trace	0	0.7	3.6	2.9	2.1	2.8	1.9	3.3	1.8
Feldspar	0	0.9	0	0	0	0	0	0	0	0	0	0	0	0	0
Carbonate	9.2	9.8	4.0	trace	0	5.5	10.2	31.1	12.6	6.1	22.0	6.5	0.0	5.0	11.5
Total cement	9.6	10.7	5.7	0	0	5.5	10.2	31.8	16.2	9	24.1	9.3	1.9	8.3	13.3
Total of all constituents	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

	Belden For	rmation			Maroon Fo	ormation					
	BS-1B siltstone to fine ss	BS-3B fine ss	BS-10E fine ss	BS-16A fine to coarse ss	M1A fine to coarse ss	M2D fine to coarse ss	M3 fine ss	M30A fine to coarse ss	M30B siltstone fine ss	M31B fine to coarse ss	
Quartz											
Monocrystalline- nonundulatory	44.4	23.5	31.2	42.7	23.0	14.6	33.7	27.2	15.4	21.3	
Monocrystalline- undulatory	0.5	6.6	2.0	24.7	1.0	2.1	2.8	4.2	4.0	11.2	
Polycrystalline	0	2.7	0.8	4.0	0	2.5	0	0	0	3.6	
Total quartz	44.9	32.8	34.0	71.4	24.0	19.2	36.5	31.4	19.4	36.1	
Feldspar											
Plagioclase	18.2	31.9	7.1	4.0	32.7	18.9	29.8	23.0	10.9	23.9	
Alkali feldspar	1.0	0.4	24.9	0	20.4	12.1	23.2	8.9	7.4	14.2	
Total feldspar	19.2	32.3	32.0	4.0	53.1	31.0	53.0	31.9	18.3	38.1	
Rock fragments	0	0	0.4	0	0	0	0	0	0	0	
Other minerals											
Muscovite	2.5	0.4	0.8	trace	1.5	18.6	0	0.5	4.5	2.5	
Biotite or chlorite	1.0	11.1	0.4	trace	0	6.8	trace	1.1	8.4	6.6	
Opaques	2.0	0	0	0	2.6	trace	trace	0.5	1.0	0	
Miscellaneous	trace	trace	trace	0	trace	0	trace	trace	trace	0.4	
Total other minerals	5.5	11.5	1.2	0	4.1	25.4	0	2.1	13.9	9.5	
Matrix											
Hematitic clay	3.5	2.2	0	4.7	3.1	3.9	2.2	4.7	22.8	5.1	
Clay	14.7	16.8	0	11.3	4.1	6.8	1.1	1.6	0	3.6	
Total clay	18.2	19.0	0	16.0	7.2	10.7	3.3	6.3	22.8	8.7	
Cement											
Quartz	2.0	4.4	3.6	8.6	3.4	1.8	1.7	4.2	1.5	6.1	
eldspar	0	0	0	0	0	0	0	0	0	0	
Carbonate	10.2	0	28.8	0	8.2	11.9	5.5	24.1	24.1	1.5	
Total cement	12.2	4.4	32.4	8.6	11.6	13.7	7.2	28.3	25.6	7.6	
Total of all constituents	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	

sults on standard rocks continue to agree with those obtained by other analysts (Cullers et al., 1985, 1987). The precision of the major elements is normally better than 6%; the precision of most of the trace elements is better than 5%. The exceptions are Yb and Lu, and their precision is normally better than 7%.

4. Results

4.1. Mineralogy

Mineralogy has been determined on representative fine to coarse sandstones (Table 1; Fig. 3). Sandstones are mostly arkosic with quartz, feldspar, and occasionally clay minerals being the major constituents. There are little or no lithic fragments in

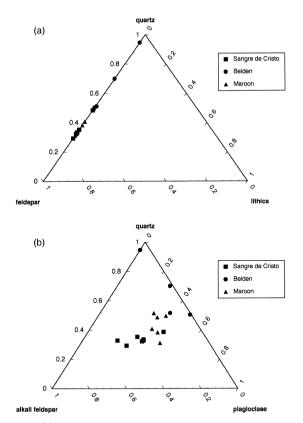


Fig. 3. (a) The relative amounts of quartz, feldspar, and lithics found in the sandstones (top). (b) The relative amounts of quartz, alkali feldspar, and plagioclase found in the sandstones (bottom).

these rocks. The Sangre de Cristo and Maroon formations contain similar ratios of quartz to total feldspar (Fig. 3a). Moreover, these ratios are similar to those in granitoids or granite gneisses, suggesting minimal chemical weathering of these units. In contrast, the sandstones of the Belden Formation have a higher quartz/total feldspar ratio than do those of the Sangre de Cristo and Maroon formations (Fig. 3a). This suggests that detritus in the Belden was weathered enough to have removed more of the feldspar from the original granitoid sources than the other two formations or that it was derived from recycled sedimentary rocks (Suttner and Dutta, 1986).

The alkali feldspar to plagioclase ratio increases from the Belden to the Maroon to the Sangre de Cristo Formations, suggesting differences in degree of weathering or source rock composition. If the Belden Formation has a high quartz to total feldspar ratio due to more weathering than in the other two formations, then the greater abundance of plagioclase relative to alkali feldspar in the Belden may be due to source rock composition as plagioclase generally weathers more readily than alkali feldspar (Nesbitt and Markovics, 1997). This interpretation will be seen to be consistent with the chemical index of weathering of these units as discussed later.

4.2. Element compositions

The elemental compositions of individual samples are given in Tables 2–7, and the averages of the elemental compositions relative to Al_2O_3 are provided in Table 8. The average of the elemental concentrations to Al_2O_3 of the medium to coarse sandstones and the siltstones to fine sandstones in the Sangre de Cristo Formation are compared to those of shales from the same formation in Fig. 4.

The elemental concentrations to Al_2O_3 ratios of the sample averages have been taken to the log_{10} to compare them statistically in order to avoid the constant sum problem (Cardenas et al., 1996). This procedure converts the original data of constant sums to continuous variables that can range up to infinity. This procedure thus allows data to be compared using parametric tests such as the Student's *t*-test. The log of ratios of Fe_2O_3 , MgO, Rb, Th, Co, Sc, Cr, Cs and most of the REE to Al_2O_3 are signifi-

Table 2
Major and trace element compositions of the shales and sandstones

Element	Sangre de	Cristo Form	ation						
	SDC-1 shale	SDC-2 shale	SDC-3 siltstone	SDC-4 fine ss	SDC-5 medium to coarse ss	SDC-6 medium to coarse ss	SDC-7 silt to fine ss	SDC-8 silt to fine ss	SDC-9 shale
SiO ₂	45.4	50.6	36.0	60.7	67.0	65.2	59.5	60.3	55.1
Al_2O_3	13.1	14.6	8.72	13.5	13.5	14.8	16.6	17.3	14.4
Fe_2O_3	5.64	5.61	5.29	2.66	3.74	5.34	6.57	6.03	5.59
MnO	0.15	0.12	0.35	0.17	0.047	0.027	0.036	0.030	0.10
MgO	5.53	4.92	5.31	2.40	2.24	3.03	4.14	3.96	3.77
CaO	11.45	6.72	20.62	6.49	2.14	0.87	0.80	0.73	5.96
Na ₂ O	1.06	1.16	0.89	2.87	3.13	3.22	2.79	2.39	2.37
K ₂ O	3.47	4.90	2.37	4.44	4.69	4.95	5.65	5.65	4.79
$\overline{\text{TiO}}_2$	0.77	0.72	0.51	0.60	0.41	0.71	0.95	0.92	0.90
LOI	13.76	10.52	19.73	6.69	3.06	2.50	3.13	3.37	7.45
Total	100.33	99.87	99.8	100.52	99.96	100.65	100.17	100.68	100.43
Rb	127	139	91	107	118	126	146	150	128
Ba	459	438	367	777	928	914	843	773	675
Sr	494	252	421	274	153	140	112	101	166
Th	15.3	19.2	9.1	9.2	6.9	14.8	26.0	24.6	23.8
Hf	3.8	3.2	2.3	4.5	4.6	8.0	9.0	7.9	9.9
Ta	1.9	2.5	1.2	2.2	1.8	3.1	3.6	3.6	4.3
Co	13.7	12.7	14.4	7.8	6.0	8.2	10.5	9.7	9.6
Sc	14.2	18.2	9.0	12.9	6.1	9.4	14.6	16.2	14.9
Cr	65	61	44	37	42	37	68	57	49
Cs	4.6	4.1	3.2	1.4	0.4	0.6	1.5	2.0	2.0
La	68.8	139	48.3	60.7	35.8	58.1	148	126	113
Ce	121	249	91.9	109	65	108	268	172	209
Sm	12.1	18.5	8.32	9.23	5.48	8.71	20.6	17.0	17.4
Eu	1.72	2.31	1.34	1.54	1.31	1.52	3.35	2.20	2.67
Tb	1.36	1.49	1.02	1.16	0.73	0.99	1.69	1.19	2.06
Yb	4.37	4.52	2.79	3.92	3.04	4.32	5.81	5.39	7.00
Lu	0.79	0.70	0.46	0.74	0.43	0.66	0.80	0.75	1.02
Eu/Eu*	0.49	0.49	0.55	0.57	0.79	0.61	0.627	0.549	0.534
(La/Lu)cn	8.7	19.7	10.5	8.2	8.3	8.8	18.4	16.9	11.1
La/Sc	4.85	7.64	5.37	4.71	5.87	6.18	10.14	7.78	7.58
Th/Sc	1.08	1.05	1.01	0.71	1.13	1.57	1.78	1.52	1.60
La/Co	5.02	10.94	3.35	7.78	5.97	7.09	14.10	12.99	11.77
Th/Co	1.12	1.51	0.63	1.18	1.15	1.80	2.48	2.54	2.48
La/Cr	1.06	2.28	1.10	1.64	0.85	1.57	2.18	2.21	2.31
Th/Cr	0.24	0.31	0.21	0.25	0.16	0.40	0.38	0.43	0.49
CIW'-1	0.883	0.884	0.856	0.741	0.724	0.736	0.783	0.815	0.787

cantly lower in the medium to coarse sandstones than those of the shales in the Sangre de Cristo Formation (Fig. 4a) using the Student's *t*-test or Welch test depending on whether the standard deviations between comparison sets are likely the same or different, respectively. The log of ratios of SiO₂, Na₂O, Ba, and Hf to Al₂O₃ are significantly higher in the medium to coarse sandstones than in the

shales. This difference must at least partially be due to the higher quartz and feldspar (concentrate Si, Na, Ba, and dilute many other elements) relative to clay and ferromagnesian minerals (concentrate Fe, Mg, Co, Cr) in the medium to coarse sandstones relative to the shales. Also the Eu/Eu* of the medium to coarse sandstones is higher than in the shales, presumably due to higher amounts of feldspar (high

Table 3
Major and trace element compositions of the shales and sandstones

Element	Sangre de C	risto Formatio	1					
	SDC-10 silt to fine ss	SDC-11 shale	SDC-12 silt to fine ss	SDC-13 medium to coarse ss	SDC-18 fine to medium ss	SDC-19 very fine to fine ss	SDC-20 shale	SDC-21 fine to coarse ss
SiO ₂	49.1	55.4	53.7	51.6	53.7	62.4	50.1	63.1
Al_2O_3	12.4	13.0	13.1	10.8	6.4	12.9	12.1	13.5
Fe_2O_3	6.59	5.42	5.31	3.12	2.01	2.83	4.56	3.17
MnO	0.19	0.11	0.15	0.24	0.32	0.094	0.096	0.076
MgO	3.44	3.69	2.41	1.76	2.14	2.55	5.05	1.58
CaO	10.36	7.20	8.69	13.22	15.94	5.39	9.16	4.56
Na ₂ O	2.28	2.43	2.99	2.65	0.10	3.23	1.06	3.69
K ₂ O	3.87	4.08	4.19	3.62	2.43	3.12	3.96	4.09
$\Gamma i O_2$	0.70	0.77	0.81	0.55	0.59	0.64	0.78	0.45
LOI	10.71	8.38	8.25	12.27	15.54	5.97	12.46	4.90
Total	99.64	100.5	99.6	99.83	99.17	99.12	99.33	99.12
Rb	104	111	107	93	70	75	123	101
Ва	631	619	675	771	369	751	534	916
Sr	153	174	170	238	197	191	174	168
Γh	19.3	17.0	16.8	11.4	9.7	8.4	18.8	7.9
Hf	6.2	7.5	13.5	8.7	11.8	8.2	5.7	7.0
Га	3.1	2.9	4.2	2.4	1.4	2.6	2.7	2.8
Co	11.3	10.1	6.5	5.7	3.5	2.8	12.7	5.3
Sc	12.0	13.3	10.9	8.5	6.2	9.9	14.2	6.4
Cr	44	48	35	36	41	34	69	25
Cs	2.3	1.6	0.94	1.2	1.1	0.3	3.9	0.4
La	107	98.1	71.7	80.8	47.6	30.1	73.6	44.2
Ce	200	184	132	179	97.9	62	149	87.8
Sm	14.9	15.5	11.8	14.1	7.62	5.10	11.1	7.26
Eu	2.20	2.24	1.94	2.82	1.32	1.18	1.81	1.72
ГЬ	1.68	1.80	1.66	1.93	1.02	0.78	1.35	1.02
Yb	5.20	5.44	6.50	5.19	3.46	2.92	4.10	4.02
Lu	0.79	0.82	0.93	0.76	0.55	0.53	0.78	0.58
Eu/Eu*	0.51	0.517	0.525	0.66	0.569	0.698	0.55	0.77
La/Lu)cn	13.6	12.0	7.7	10.6	8.6	5.7	9.4	7.6
La/Sc	8.92	7.38	6.58	9.51	7.68	3.04	5.18	6.91
Th/Sc	1.61	1.28	1.54	1.34	1.56	0.85	1.32	1.23
.a/Co	9.47	9.71	11.03	14.18	13.60	10.75	5.80	8.34
Γh/Co	1.71	1.68	2.58	2.00	2.77	3.00	1.48	1.49
La/Cr	2.43	2.04	2.05	2.24	1.16	0.89	1.07	1.77
Γh/Cr	0.44	0.35	0.48	0.32	0.24	0.25	0.27	0.32
CIW'-1	0.768	0.765	0.727	0.712	0.975	0.708	0.874	0.690

Eu/Eu*) and lower amounts of ferromagnesian minerals and clay minerals (low Eu/Eu*) in the sandstones relative to the shales. Other ratios are not significantly different.

There is less difference in the composition of the siltstone to fine sandstone fraction relative to shales in the Sangre de Cristo Formation than in the medium to coarse sandstones relative to shales (Fig. 4b).

Only the log of ratios of MgO, Co, and Sc relative to Al_2O_3 are lower and Na_2O , Ba, and Hf to are higher in the siltstones to fine sandstones relative to shales. The logs of other ratios are not significantly different. Weathering may have removed more Na and Ba from the clays composing the shales than from the minerals composing the siltstones and fine sandstones. Ferromagnesian minerals may be more con-

Table 4
Major and trace element compositions of the shales and sandstones

Element	Sangre de Crist	o Formation					
	SDC-22 medium to coarse ss	SDC-23 siltstone to fine ss	SDC-24 siltstone to fine ss	SDC-25 medium to coarse ss	SDC-26 siltstone to fine ss	SDC-27 siltstone	SDC-28 fine ss
SiO_2	57.8	55.5	62.0	72.9	60.6	53.0	57.6
Al_2O_3	12.3	10.3	14.0	12.0	11.7	15.7	13.2
Fe_2O_3	4.28	5.09	5.32	4.77	4.86	7.32	5.37
MnO	0.33	0.17	0.12	0.061	0.084	0.12	0.19
MgO	2.44	2.40	3.28	0.94	4.59	4.53	3.85
CaO	7.31	10.32	3.44	0.38	3.69	3.16	4.19
Na ₂ O	3.24	0.93	2.18	3.49	1.97	1.54	2.62
K ₂ O	2.78	2.81	3.65	3.67	4.09	6.43	4.75
TiO_2	0.83	0.65	0.89	0.65	0.76	0.82	0.81
LOI	8.08	11.14	5.46	1.04	7.19	7.51	7.28
Total	99.39	99.31	100.3	99.90	99.53	100.13	99.86
Rb	92	110	113	87	108	157	126
Ba	745	339	487	1966	645	706	806
Sr	175	215	145	173	122	116	139
Th	12.2	12.4	15.2	8.8	13.8	39.7	22.7
Hf	13.2	6.0	11.5	8.6	10.9	6.7	12.3
Та	3.5	1.4	2.7	4.1	3.5	5.3	5.0
Co	7.4	11.3	11.4	3.8	7.2	8.7	7.3
Sc	13.4	10.6	13.0	5.2	11.1	18.2	12.3
Cr	46	64	61	25	52	53	36
Cs	1.2	4.2	2.4	0.35	1.7	3.0	1.3
La	56.7	61.2	59.3	26.5	46.8	269	79.8
Ce	120	106	121	49.7	98.2	494	163
Sm	11.1	10.2	8.8	4.07	8.31	37.7	14.9
Eu	2.13	1.60	1.59	1.05	1.41	4.82	2.02
Tb	1.61	1.17	0.98	0.68	1.11	3.46	1.55
Yb	4.98	3.92	4.39	4.23	4.87	10.1	6.43
Lu	0.75	0.54	0.61	0.59	0.68	1.30	0.87
Eu/Eu*	0.61	0.55	0.635	0.804	0.561	0.471	0.493
(La/Lu)cn	7.5	11.3	9.8	4.5	6.9	20.8	9.2
La/Sc	4.23	5.77	4.56	5.10	4.22	14.78	6.49
Th/Sc	0.91	1.17	1.17	1.69	1.24	2.18	1.85
La/Co	7.66	5.42	5.20	6.97	6.50	30.92	10.93
Th/Co	1.65	1.10	1.33	2.32	1.92	4.56	3.11
La/Cr	1.23	0.96	0.97	1.06	0.90	5.08	2.22
Th/Cr	0.27	0.19	0.25	0.35	0.27	0.75	0.63
CIW'-1	0.698	0.871	0.796	0.676	0.783	0.861	0.754

centrated in the shales than in the siltstone to fine sandstone fraction thus increasing the amount of MgO, Co, and Sc. Elemental ratios critical of the source rock composition, such as La/Sc, Th/Sc, La/Co, Th/Co, Th/Cr, and Eu/Eu*, are not significantly different in the shales and the siltstones to fine sandstones.

The Belden Formation has the fewest analyzed samples, and this formation varies the most of any

formation in terms of the percent carbonate and the feldspar/quartz ratio (Tables 2–8). Thus, the chemical composition of samples from the Belden Formation also varies more than the Sangre de Cristo and Maroon formations. Most of the logs of elemental concentrations to Al_2O_3 ratios of sandstones of the Belden are the same as the shales and siltstones. Only the log of Na_2O and Cs to Al_2O_3 ratios are significantly higher in the sandstones relative to the

Table 5
Major and trace element compositions of the shales and sandstones

Element	Belden Fo	ormation									
	BS-2B shale	BS-2A shale	BS-1B siltstone to fine ss	BS-1A shale	BS-3B fine ss	BS-3A shale	BS-10A shale	BS-10B fine ss	BS-15 shale	BS-16A fine to coarse ss	BS-16B shale
$\overline{\text{SiO}_2}$	48.8	55.2	68.5	58.6	65.6	46.9	65.1	51.7	24.9	91.0	31.6
Al_2O_3	19.5	19.3	7.9	17.6	14.7	21.7	10.3	5.9	9.5	3.8	13.1
Fe_2O_3	10.32	6.73	4.01	4.53	8.52	5.72	2.78	1.49	2.80	2.63	4.69
MnO	0.020	0.032	0.040	0.013	0.017	0.029	0.024	0.060	0.063	0.067	0.086
MgO	6.05	4.12	2.33	2.61	2.84	3.62	5.28	5.94	12.67	0.15	9.08
CaO	1.00	1.92	7.10	2.07	0.52	5.02	4.00	13.82	19.22	0.10	13.90
Na ₂ O	0.47	0.51	2.32	0.52	3.22	0.81	0.74	0.97	0.27	0.03	0.312
K ₂ O	3.04	4.28	0.17	2.56	0.38	3.93	3.62	3.16	0.74	0.87	3.63
TiO_2	1.00	0.86	0.43	1.07	0.75	1.13	0.49	0.27	0.41	0.17	0.59
LOI	9.83	6.95	7.59	10.61	3.41	11.47	7.97	16.81	29.51	1.50	22.49
Total	100.03	99.90	100.39	100.18	99.96	100.33	100.30	100.12	100.08	100.32	99.29
Rb	100	170	13	104	23	180	118	76	43	27	139
Ba	281	296	73	286	104	391	319	371	78	189	391
Sr	104	121	177	107	112	365	69	99	155	78	101
Γh	30.0	23.5	12.7	22.9	11.2	23.1	8.3	8.5	9.3	14.7	19.0
Hf	2.8	1.3	27.2	6.6	10.6	3.0	8.5	11.5	2.3	3.2	3.2
Та	_	_	1.3	2.7	1.7	_	0.94	0.67	0.89	0.55	1.9
Co	28.6	15.2	5.3	8.6	8.7	6.6	4.5	2.1	7.3	9.8	12.0
Sc	23.6	19.9	7.4	18.4	11.7	25.5	8.8	4.0	10.2	1.9	11.9
Cr	76	86	26	143	78	126	60	20	47	14	94
Cs	10.6	7.0	0.3	3.9	0.34	6.1	7.7	1.2	8.0	0.53	11.9
La	104	86.3	23.6	71.7	29.5	97.1	34.3	25.8	23.0	16.3	30.7
Ce	233	176	59.1	149	69.7	161	62.2	44.3	44.2	32.4	59
Sm	22.6	19.7	7.24	11.2	5.18	15.2	5.54	4.69	3.65	3.95	4.84
Eu	2.42	2.85	1.12	1.47	1.15	1.48	0.87	0.74	0.61	0.55	0.80
Гb	2.28	1.97	1.51	1.23	0.77	1.17	0.54	0.57	0.41	0.80	0.52
Yb	7.13	4.57	6.62	5.12	3.27	4.58	2.20	2.67	1.80	2.15	2.30
Lu	0.98	0.75	0.93	0.75	0.50	0.71	0.33	0.42	0.27	0.31	0.34
Eu/Eu*	0.385	0.53	0.44	0.46	0.69	0.39	0.39	0.52	0.57	0.39	0.58
(La/Lu)c	n 10.6	11.6	2.6	9.5	5.9	13.7	10.4	6.2	8.5	5.2	8.9
La/Sc	4.41	4.34	3.19	3.90	2.52	3.81	3.90	6.45	2.25	8.58	2.58
Γh/Sc	1.27	1.18	1.72	1.24	0.96	0.91	0.94	2.13	0.91	7.74	1.60
La/Co	3.64	5.68	4.45	8.34	3.39	14.71	7.62	12.29	3.15	1.66	2.56
Th/Co	1.05	1.55	2.40	2.66	1.29	3.50	1.84	4.05	1.27	1.50	1.58
La/Cr	1.37	1.00	0.91	0.50	0.38	0.77	0.57	1.29	0.49	1.16	0.33
Th/Cr	0.39	0.27	0.49	0.16	0.14	0.18	0.14	0.43	0.20	1.05	0.20
CIW'-1	0.962	0.958	0.674	0.954	0.735	0.942	0.894	0.787	0.955	0.987	0.985

shales, and only the $\mathrm{Sc/Al_2O_3}$ ratio is significantly lower in the sandstones relative to shales. This similarity in composition between the sandstones and the shales and siltstones is probably an artifact of the large variability in mineralogic composition and the relatively few samples analyzed.

The ratios of the log of Fe_2O_3 , MgO, TiO_2 , Ba, and Cr to Al_2O_3 are significantly lower in the fine to

medium sandstones relative to the shales of the Maroon Formation (Fig. 5a). The log of other ratios is not significantly different. The lower ratios of ${\rm Fe_2O_3}$, MgO, ${\rm TiO_2}$, Ba, and Cr to ${\rm Al_2O_3}$ in the coarser fractions than the fine fractions are likely due to depletion in biotite or other ferromagnesian minerals in the former than the latter. The log ratio of elemental concentrations to ${\rm Al_2O_3}$ of the siltstones

Table 6
Major and trace element compositions of the shales and sandstones

Element	Maroon F	ormation							
	M1A fine ss	M1B siltstone	M2A siltstone to fine ss	M2B siltstone	M2D fine to coarse ss	M3 fine ss	M30A very fine to coarse ss	M31B fine to coarse ss	M31A siltstone to fine ss
SiO ₂	61.1	60.4	65.8	69.5	60.8	69.1	67.0	74.6	66.6
Al_2O_3	12.5	12.7	10.2	10.2	13.8	10.8	8.0	9.8	13.9
Fe_2O_3	3.14	4.21	3.71	3.37	2.72	2.99	1.96	1.68	4.99
MnO	0.10	0.12	0.052	0.068	0.11	0.098	0.049	0.030	0.032
MgO	0.77	1.36	1.87	1.37	1.20	1.34	0.65	0.51	1.48
CaO	8.34	7.02	6.94	5.24	5.55	4.82	9.40	3.46	2.17
Na ₂ O	4.37	3.87	1.64	1.83	2.32	2.68	1.76	1.91	1.55
K ₂ O	2.00	2.49	1.95	2.03	4.03	2.93	2.03	3.20	4.64
TiO_2	0.63	0.62	0.63	0.69	0.36	0.68	0.40	0.24	0.53
LOI	6.96	6.84	7.68	6.15	8.25	5.15	8.86	3.79	3.90
Total	99.91	99.63	100.47	100.45	99.14	100.59	100.11	99.22	99.79
Rb	56	77	90	87	274	69	73	118	175
Ba	65	461	910	336	304	596	3.57	399	504
Sr	160	186	124	103	134	146	155	127	103
Th	7.1	9.4	10.2	10.9	12.3	10.1	9.3	7.9	14.8
Hf	8.2	6.9	8.5	9.2	2.4	12.4	8.4	3.4	6.3
Ta	2.2	2.1	1.2	1.3	4.3	1.4	0.81	0.8	1.5
Co	3.3	5.2	0.99	7.5	4.7	6.7	2.7	2.0	8.3
Sc	11.4	12.4	8.5	8.5	14.1	9.6	5.4	5.0	10.3
Cr	25	37	60	63	26	55	45	17	37
Cs	0.50	1.8	3.8	3.3	9.3	1.1	2.5	4.8	14
La	51.0	64.2	31.2	29.1	35.8	21.5	26.3	24.7	37.5
Ce	92.0	118	59	56.7	67.5	42.2	48.2	46.9	68.9
Sm	8.45	9.92	5.56	5.32	5.90	4.47	4.77	4.61	6.20
Eu	1.77	1.79	1.00	0.95	0.61	0.99	0.78	0.90	0.95
Tb	1.18	1.18	0.64	0.73	0.62	0.68	0.56	0.51	0.74
Yb	4.33	4.64	2.71	2.95	2.39	3.53	2.32	1.73	3.00
Lu	0.64	0.69	0.43	0.48	0.35	0.52	0.36	0.27	0.43
Eu/Eu*	0.66	0.60	0.61	0.59	0.36	0.69	0.57	0.69	0.52
(La/Lu)cn	8.0	9.3	7.3	6.1	10.2	4.1	7.3	9.2	8.7
La/Sc	4.47	5.18	3.67	3.42	2.54	2.24	4.87	4.94	3.64
Th/Sc	0.62	0.76	1.20	1.28	0.87	1.05	1.72	1.58	1.44
La/Co	15.45	12.35	31.52	3.88	7.62	3.21	9.74	12.35	4.52
Th/Co	2.15	1.81	10.30	1.45	2.62	1.51	3.44	3.95	1.78
La/Cr	2.04	1.74	0.52	0.46	1.38	0.39	0.58	1.45	1.01
Th/Cr	0.28	0.25	0.17	0.17	0.47	0.18	0.21	0.46	0.40
CIW'-1	0.635	0.666	0.791	0.772	0.783	0.710	0.734	0.757	0.845

to fine sandstones relative to shales are all statistically the same, suggesting a similar provenance signature in both kinds of sediment.

Variation in major element compositions due to mineralogical differences can be illustrated in plots of elemental compositions (Fig. 6). The composition of shales from the Sangre de Cristo Formation tends to overlap and lie in positions intermediate between those of the Belden and Maroon Formations in plots of SiO₂ vs. Al₂O₃. This is consistent with the shales from the Sangre de Cristo Formation containing intermediate amounts of quartz, feldspar, clay minerals, biotite, opaque minerals, hematite, and calcite between those of the Belden and Maroon formations.

Table 7
Major and trace element compositions of the shales and sandstones

Element	Maroon Fo	rmation							Maroon Formation										
	M30D siltstone to fine ss	M30C siltstone to fine ss	M30B siltstone to fine ss	M91 siltstone	M50A medium to coarse ss	M50B siltstone to fine ss	M90 siltstone to fine ss	M92A siltstone to fine ss	M92B shale										
SiO ₂	46.9	43.6	64.2	57.6	73.8	70.0	70.4	63.1	61.3										
Al_2O_3	9.1	5.9	8.3	9.2	9.2	10.7	11.0	10.5	13.7										
Fe_2O_3	2.50	1.83	2.06	3.32	1.72	2.54	5.81	3.29	4.82										
MnO	0.067	0.077	0.052	0.12	0.049	0.076	0.042	0.070	0.065										
MgO	0.86	0.92	1.00	1.86	0.42	1.15	1.07	2.77	2.93										
CaO	18.41	23.47	10.11	12.31	4.71	5.30	1.94	7.44	4.58										
Na ₂ O	2.05	0.92	1.68	1.37	2.88	2.75	2.92	1.87	1.83										
K ₂ O	1.95	1.68	2.20	1.86	2.19	1.86	2.92	2.77	3.71										
TiO ₂	0.48	0.38	0.39	0.60	0.13	0.26	1.09	0.55	0.78										
LOI	16.70	21.00	9.90	12.29	4.26	5.43	2.05	7.93	6.62										
Total	99.02	99.78	99.89	100.53	99.36	100.07	99.24	100.29	100.34										
Rb	87	72	83	83	76	81	82	91	117										
Ba	310	321	429	504	401	310	572	347	421										
Sr	280	277	158	127	158	150	158	131	127										
Th	10.6	5.8	6.4	10.1	3.4	6.4	21	7.5	10.7										
Hf	6.4	4.9	5.2	10.3	2.0	3.7	32.0	5.4	6.7										
Ta	0.85	0.63	0.74	1.2	0.21	0.46	1.7	0.86	1.2										
Co	3.1	3.9	5.5	8.2	3.5	3.4	5.5	9.2	14.8										
Sc	5.6	4.6	5.4	8.0	5.9	7.2	10.6	8.3	12.6										
Cr	33	36	39	49	15	38	66	49	70										
Cs	3.0	2.7	3.1	3.6	0.91	1.4	2.1	4.2	6.5										
La	35.0	26.9	28.3	34.8	14.4	88.8	48.4	21.0	31.0										
Ce	58.6	49.6	52.8	65.5	27.5	119	90.9	45.5	70										
Sm	5.85	4.84	5.46	6.44	3.33	4.53	8.48	4.30	6.41										
Eu	0.94	0.73	0.78	1.27	0.66	0.81	1.06	0.87	1.28										
Tb	0.79	0.57	0.57	0.90	0.38	0.49	1.20	0.62	0.87										
Yb	3.37	2.40	2.43	3.59	1.17	1.48	5.62	2.19	2.87										
Lu	0.50	0.34	0.36	0.55	0.18	0.21	0.87	0.29	0.41										
Eu/Eu*	0.52	0.51	0.51	0.63	0.69	0.62	0.41	0.64	0.65										
(La/Lu)cn	7.0	7.8	7.9	6.4	8.0	42.1	5.5	7.1	7.5										
La/Sc	6.25	5.85	5.24	4.35	2.44	12.33	4.57	2.53	2.46										
Th/Sc	1.89	1.26	1.19	1.26	0.58	0.89	1.98	0.90	0.85										
La/Co	11.29	6.90	5.15	4.24	4.11	26.12	8.80	2.28	2.09										
Th/Co	3.42	1.49	1.16	1.23	0.97	1.88	3.82	0.82	0.72										
La/Cr	1.06	0.75	0.73	0.71	0.96	2.34	0.73	0.43	0.44										
Th/Cr	0.32	0.16	0.16	0.21	0.23	0.17	0.32	0.15	0.15										
CIW'-1	0.730	0.796	0.750	0.803	0.660	0.703	0.696	0.773	0.820										

The samples from the Sangre de Cristo Formation have relatively constant SiO_2/Al_2O_3 ratios, but vary in the direction toward the 0% SiO_2 and Al_2O_3 corner (Fig. 6a). This suggests that much of the chemical variation is due to dilution of minerals with no SiO_2 and Al_2O_3 (hematite, calcite, or opaque minerals) combined with minerals that overall pro-

duce a constant SiO₂/Al₂O₃ ratio. In the Fe₂O₃ vs. Al₂O₃ plot, there is a lot of variation of rocks in the Sangre de Cristo Formation between calcite–quartz, hematite–magnetite, and layer silicate (clay minerals and biotite)–feldspar end members, suggesting that much of the variation in this plot is due to variation in these minerals.

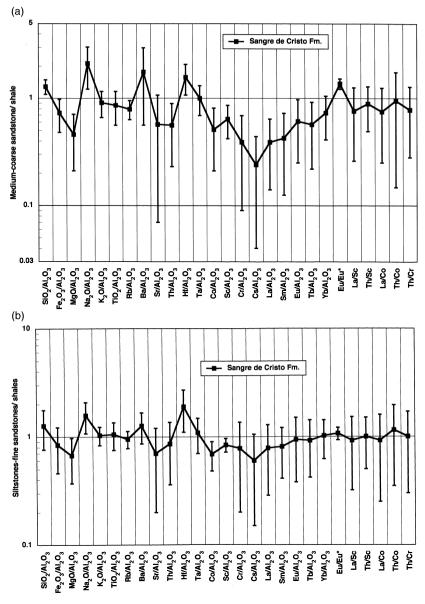


Fig. 4. (a) The ratio of the average elemental concentration to Al_2O_3 in the medium-coarse sandstones are compared to those in shales from the Sangre de Cristo Formation. The error bars represent the range of one standard deviation from the mean (top). (b) The ratio of the average elemental concentration to Al_2O_3 in the siltstones—fine sandstones from the Sangre de Cristo Formation are compared to those in shales (bottom).

The sandstones and shales of the Belden Formation have the largest compositional difference of any of the units (Fig. 6). The shales of the Belden Formation have the lowest SiO_2 relative to Al_2O_3 compared to those of the Sangre de Cristo and

Maroon formations; the sandstones have the highest SiO_2 relative to Al_2O_3 compared to those of the other units. The low SiO_2/Al_2O_3 ratios of the shales in the Belden Formation are likely due to the enriched Al-rich clay minerals like kaolinite or illite

relative to quartz. The high quartz relative to other minerals in the sandstones of the Belden Formation would produce the high $\mathrm{SiO}_2/\mathrm{Al}_2\mathrm{O}_3$ ratios. Again some of the shales and sandstones of the Belden Formation, like the Sangre de Cristo Formation, are skewed toward the 0% SiO_2 and $\mathrm{Al}_2\mathrm{O}_3$ (Fig. 6a) consistent with enrichment in calcite or Fe-rich minerals. The samples with the lowest SiO_2 and $\mathrm{Al}_2\mathrm{O}_3$ also contain the highest CaO and LOI so is consistent with calcite being the most likely reason for this elemental correlation.

The shales from the Maroon Formation have the highest SiO₂/Al₂O₃ ratios of any of the shales (Fig. 6a; Table 8). This is likely due to less Al-rich clay minerals and feldspar and more quartz in the shales of the Maroon Formation compared to those of

Sangre de Cristo and Belden Formations. The ${\rm SiO_2/Al_2O_3}$ ratios of the sandstones, however, are intermediate between those of the other formations. This suggests that there is an intermediate amount of quartz relative to feldspar in the Maroon Formation compared to the Sangre de Cristo and Belden Formations as is observed.

4.3. CIW'

Various indices of weathering have been proposed based on different molecular proportions of mobile element oxides (Na₂O, CaO, MgO, K₂O) relative to immobile element oxides, Al₂O₃, ZrO₂, and TiO₂ (Chittleborough, 1991). For example, the chemical index of weathering (CIW = $[Al_2O_3/(Al_2O_3 + CaO)]$

Table 8

The mean elemental concentration ratios and standard deviations of sediments in the Sangre de Cristo Belden, and Maroon Formations.

Elemental ratios	Sangre de Cristo F	ormation		Belden Formation		
	Shale to siltstone (7) ^b	Siltstone to fine sandstone (10)	Medium to coarse sandstone (7)	Shale to siltstone (5)	Shale to limestone (2)	Fine to medium sandstone (4)
SiO ₂ /Al ₂ O ₃	3.8 ± 0.4	4.8 ± 1.4	4.9 ± 0.6	3.4 ± 1.7	2.52 ± 0.15	11.5 ± 8.5
Fe_2O_3/Al_2O_3	0.44 ± 0.09	0.37 ± 0.09	0.32 ± 0.07	0.33 ± 0.12	0.32 ± 0.03	0.52 ± 0.20
MgO/Al_2O_3	0.37 ± 0.12	0.25 ± 0.07	0.17 ± 0.05	0.27 ± 0.15	1.0 ± 0.45	0.40 ± 0.35
CaO/Al ₂ O ₃	0.80 ± 0.72	0.74 ± 0.73	0.26 ± 0.20	0.18 ± 0.13	$1.54 \pm .68$	0.83 ± 1.1
Na ₂ O/Al ₂ O ₃	0.11 ± 0.04	0.17 ± 0.04	0.23 ± 0.04	0.035 ± 0.02	0.017 ± 0.014	0.17 ± 0.11
K_2O/Al_2O_3	0.32 ± 0.05	0.33 ± 0.03	0.29 ± 0.05	0.21 ± 0.08	0.18 ± 0.14	0.20 ± 0.17
TiO ₂ /Al ₂ O ₃	0.058 ± 0.006	0.06 ± 0.01	0.05 ± 0.014	0.051 ± 0.006	0.044 ± 0.001	0.040 ± 0.004
Rb/Al ₂ O ₃	9.6 ± 0.7	9.1 ± 1.0	7.6 ± 1.0	7.9 ± 2.5	7.6 ± 4.3	5.8 ± 5.2
Ba/Al ₂ O ₃	42 ± 6.6	53 ± 10	74 ± 41	19 ± 7	19 ± 15	5.8 ± 5.4
Sr/Al ₂ O ₃	21 ± 15	15 ± 8	12.3 ± 2.3	8.2 ± 4.8	12 ± 6	16.8 ± 6.5
Th/Al ₂ O ₃	1.5 ± 0.55	1.3 ± 0.3	0.86 ± 0.27	1.19 ± 0.27	1.22 ± 0.33	1.92 ± 1.4
Hf/Al ₂ O ₃	0.42 ± 0.17	0.80 ± 0.44	0.66 ± 0.24	0.31 ± 0.28	0.24 ± 0.01	1.74 ± 1.3
Ta/Al ₂ O ₃	0.22 ± 0.08	0.24 ± 0.07	0.22 ± 0.07	0.12 ± 0.04	0.12 ± 0.04	0.135 ± 0.025
Co/Al ₂ O ₃	0.94 ± 0.36	0.65 ± 0.19	0.48 ± 0.20	0.70 ± 0.47	0.85 ± 0.11	1.1 ± 1
Sc/Al ₂ O ₃	1.11 ± 0.09	0.94 ± 0.06	0.72 ± 0.26	1.06 ± 0.14	0.99 ± 0.11	0.73 ± 0.19
Cr/Al ₂ O ₃	4.3 ± 0.09	3.9 ± 1.4	2.9 ± 0.90	5.6 ± 1.6	6.1 ± 1.6	3.9 ± 0.9
Cs/Al ₂ O ₃	0.25 ± 0.10	0.15 ± 0.10	0.06 ± 0.05	0.43 ± 0.22	0.88 ± 0.05	0.10 ± 0.08
La/Al ₂ O ₃	8.4 ± 4.1	6.6 ± 1.7	3.3 ± 1.0	4.3 ± 0.3	2.4 ± 0.1	3.4 ± 1.1
Sm/Al ₂ O ₃	1.27 ± 0.52	1.03 ± 0.22	0.54 ± 0.19	0.81 ± 0.27	0.38 ± 0.01	0.78 ± 0.30
Eu/Al ₂ O ₃	0.18 ± 0.06	0.17 ± 0.05	0.11 ± 0.03	0.101 ± 0.033	0.063 ± 0.002	0.122 ± 0.030
Tb/Al ₂ O ₃	0.13 ± 0.04	0.12 ± 0.03	0.74 ± 0.03	0.078 ± 0.029	0.042 ± 0.002	0.14 ± 0.076
Yb/Al ₂ O ₃	0.41 ± 0.12	0.42 ± 0.08	0.30 ± 0.06	0.26 ± 0.07	0.18 ± 0.014	0.52 ± 0.26
Eu/Eu*	0.51 ± 0.03	0.55 ± 0.04	0.70 ± 0.04	0.43 ± 0.06	0.58 ± 0.06	0.51 ± 0.13
La/Sc	7.5 ± 3.4	6.9 ± 1.9	5.7 ± 2.0	4.1 ± 0.3	2.4 ± 0.2	5.2 ± 2.9
Th/Sc	1.4 ± 0.46	1.4 ± 0.35	1.24 ± 0.29	1.1 ± 0.2	1.3 ± 0.5	3.1 ± 3
La/Co	11.1 ± 9.3	10.2 ± 3.1	8.3 ± 2.9	8.0 ± 4.2	2.9 ± 0.4	5.5 ± 4.7
Th/Co	1.9 ± 1.3	2.2 ± 0.7	1.8 ± 0.7	2.1 ± 1.0	1.54 ± 0.06	2.4 ± 1.3
Th/Cr	0.37 ± 0.19	0.37 ± 0.14	0.29 ± 0.29	0.23 ± 0.11	0.20 ± 0.11	0.53 ± 0.38
CIW' ^a	0.844 ± 0.048	0.78 ± 0.05	0.74 ± 0.10	0.942 ± 0.03	0.98 ± 0.02	0.80 ± 0.14

Table 8 (continued)

Elemental ratios	Maroon Formation	ı		Sangre de Cristo Formation	Belden Formation	Maroon Formation
	Shale to siltstone (4)	Siltstone to fine sandstone (9)	Medium to coarse sandstone (5)	All shales to fine ss (17)	All shales to siltstones (7)	All shales to fine ss (13)
SiO ₂ /Al ₂ O ₃	6.0 ± 1.0	6.1 ± 1.1	6.7 ± 1.9	4.4 ± 1.2	3.2 ± 1.5	5.8 ± 0.8
Fe_2O_3/Al_2O_3	0.35 ± 0.02	0.32 ± 0.09	0.21 ± 0.04	0.40 ± 0.10	0.33 ± 0.10	0.33 ± 0.07
MgO/Al ₂ O ₃	0.18 ± 0.04	0.13 ± 0.05	0.21 ± 0.04	0.30 ± 0.11	0.48 ± 0.4	0.15 ± 0.05
CaO/Al ₂ O ₃	0.74 ± 0.42	1.08 ± 1.2	0.62 ± 0.33	$0.77 \pm .70$	0.57 ± 0.73	0.98 ± 1.0
Na ₂ O/Al ₂ O ₃	0.16 ± 0.02	0.21 ± 0.06	0.25 ± 0.08	0.15 ± 0.05	0.030 ± 0.018	0.20 ± 0.06
K_2O/Al_2O_3	0.22 ± 0.04	0.25 ± 0.05	0.25 ± 0.06	0.33 ± 0.04	0.20 ± 0.09	0.24 ± 0.05
TiO ₂ /Al ₂ O ₃	0.064 ± 0.005	0.054 ± 0.02	0.033 ± 0.016	0.060 ± 0.01	0.050 ± 0.006	0.057 ± 0.018
Rb/Al ₂ O ₃	8.7 ± 0.2	8.9 ± 2.4	10.3 ± 5.8	9.3 ± 0.9	7.8 ± 2.7	8.9 ± 1.9
Ba/Al ₂ O ₃	52 ± 27	42 ± 11	31 ± 17	48 ± 11	19 ± 8	45 ± 17
Sr/Al ₂ O ₃	11.4 ± 2.0	19.2 ± 12	14.4 ± 4	18 ± 12	9.5 ± 5	17 ± 11
Th/Al ₂ O ₃	0.99 ± 0.14	0.98 ± 0.39	0.76 ± 0.30	1.41 ± 0.42	1.19 ± 0.26	0.99 ± 0.32
Hf/Al ₂ O ₃	0.84 ± 0.26	0.90 ± 0.79	0.49 ± 0.37	0.64 ± 0.39	0.29 ± 0.20	0.80 ± 0.24
Ta/Al ₂ O ₃	0.12 ± 0.02	0.11 ± 0.04	0.14 ± 0.11	0.23 ± 0.07	0.12 ± 0.03	0.11 ± 0.03
Co/Al ₂ O ₃	0.70 ± 0.43	0.55 ± 0.18	0.30 ± 0.07	0.77 ± 0.30	0.74 ± 0.39	0.60 ± 0.27
Sc/Al ₂ O ₃	0.86 ± 0.04	0.79 ± 0.13	0.75 ± 0.21	1.01 ± 0.11	1.04 ± 0.13	0.78 ± 0.12
Cr/Al ₂ O ₃	5.6 ± 0.5	4.4 ± 1.3	2.6 ± 1.7	4.1 ± 1.2	5.8 ± 1.5	4.7 ± 1.4
Cs/Al ₂ O ₃	0.39 ± 0.06	0.35 ± 0.28	0.32 ± 0.26	0.19 ± 0.1	0.56 ± 0.28	0.36 ± 0.21
La/Al ₂ O ₃	3.0 ± 0.6	4.0 ± 1.9	2.8 ± 0.9	7.3 ± 3.0	3.8 ± 1.1	3.7 ± 1.7
Sm/Al_2O_3	0.59 ± 0.10	0.60 ± 0.17	0.51 ± 0.13	1.1 ± 0.4	0.69 ± 0.3	0.58 ± 0.15
Eu/Al ₂ O ₃	0.11 ± 0.02	0.097 ± 0.023	0.090 ± 0.036	0.17 ± 0.05	0.090 ± 0.033	0.100 ± 0.022
Tb/Al ₂ O ₃	0.073 ± 0.016	0.075 ± 0.022	0.060 ± 0.022	0.13 ± 0.04	0.068 ± 0.030	0.075 ± 0.020
Yb/Al ₂ O ₃	0.29 ± 0.08	0.32 ± 0.11	0.22 ± 0.09	0.41 ± 0.10	0.24 ± 0.07	0.31 ± 0.10
Eu/Eu*	0.62 ± 0.03	0.56 ± 0.09	0.59 ± 0.14	0.54 ± 0.04	0.46 ± 0.08	0.58 ± 0.07
La/Sc	3.5 ± 0.8	5.3 ± 3.0	3.9 ± 1.3	7.2 ± 2.6	3.6 ± 0.84	4.9 ± 2.6
Th/Sc	1.15 ± 0.020	1.26 ± 0.44	1.08 ± 0.54	1.43 ± 0.39	1.15 ± 0.25	1.20 ± 0.46
La/Co	10.4 ± 14	9.0 ± 7.3	9.9 ± 4.4	10.6 ± 6.3	6.5 ± 4.3	9.4 ± 9.3
Th/Co	3.4 ± 4.6	2.8 ± 1.0	2.6 ± 1.2	2.1 ± 1.0	2.0 ± 0.8	2.4 ± 2.3
Th/Cr	0.18 ± 0.02	0.24 ± 0.09	0.33 ± 0.13	0.37 ± 0.16	$0.22 \pm .09$	0.22 ± 0.08
CIW' ^a	0.79 ± 0.015	0.741 ± 0.056	0.714 ± 0.064	$0.80 \pm .06$	0.95 ± 0.03	0.755 ± 0.051

 $^{^{}a}CIW' = Al_{2}O_{3}/(Al_{2}O_{3} + Na_{2}O).$

+ Na₂O)]*100) or chemical index of alteration (CIA = $[Al_2O_3/(Al_2O_3 + CaO + Na_2O + K_2O)]$ * 100) have often been used as weathering indices with higher values suggesting more intense chemical weathering (Nesbitt and Young, 1982; Harnois, 1988; Chittleborough, 1991). Unfortunately, samples that vary a lot in CaO due to variation in calcite, such as rocks observed in this study, may suggest misleading conclusions if the CIW and CIA are used to infer the degree of weathering. Thus, in this study CaO will be left out of the chemical index of weathering (CIW') so that the $\frac{CIW' = [Al_2O_3/(Al_2O_3 + Na_2O)]*100}{(Tables 2-7)}$

The CIW' of the shales to fine sandstones of the Belden Formation is significantly higher than those from the Sangre de Cristo Formation. The CIW' of the shales to fine sandstones of the Maroon Formation is significantly lower than those of the other two formations. This suggests that the intensity or duration of weathering of the shales and fine sandstones decreased in order of Belden > Sangre de Cristo > Maroon Formations. Also the quartz-rich nature of sandstones from the Belden Formation relative to those from the Maroon and Sangre de Cristo Formations is consistent with more intense weathering of the Belden source rocks.

^bNumber of samples in parentheses.

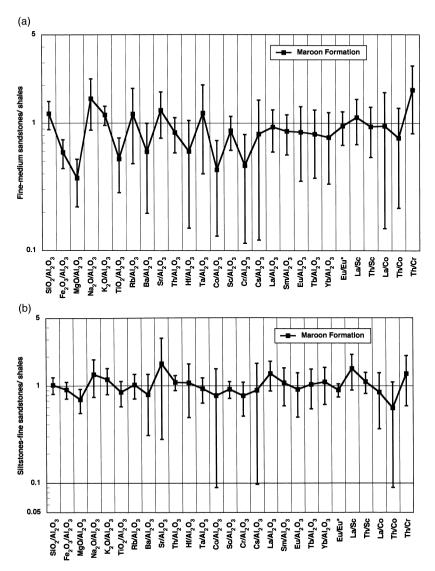


Fig. 5. (a) The ratio of the average elemental concentrations to Al_2O_3 in the fine-medium sandstones from the Maroon Formation are compared to those in shales (top). (b) The ratio of the average elemental concentrations to Al_2O_3 in the siltstones-very fine sandstones from the Sangre de Cristo Formation are compared to those in shales (bottom).

As discussed previously, the plagioclase/alkali feldspar ratio in each group of sandstones may have implications as to the degree of weathering or to source rock. If the source rocks of the Maroon and Sangre de Cristo Formation had similar ratios of plagioclase/alkali feldspar, then the higher plagioclase/alkali feldspar ratio observed in the Maroon Formation relative to the Sangre de Cristo Formation

would also suggest more intense weathering of the sandstones of the Sangre de Cristo than those from the Maroon Formation. The higher quartz/total feldspar ratio of the Belden Formation than the other two formations suggests more intense weathering of the Belden than the other formations. The presence of plagioclase as the only feldspar in the Belden Formation suggests that the source of the Belden

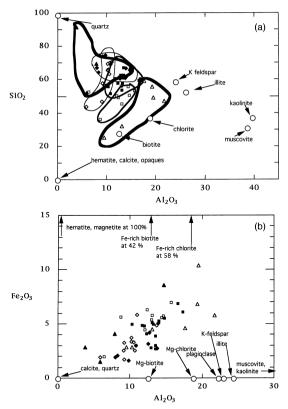


Fig. 6. (a) A plot of the weight percent of SiO_2 vs. Al_2O_3 in the samples and typical mineral compositions of observed minerals in these rocks (top; Sangre de Cristo Formation: shale = open square and sandstones = closed square and outlined in medium width line thickness; Belden Formation: shale = open triangle and sandstone = closed triangle and outlined with the thickest line; Maroon Formation: shale = open diamond and sandstone = closed diamond and outlined with the thinnest line). (b) A plot of weight percent of Fe_2O_3 vs. Al_2O_3 in the samples and typical mineral compositions of observed minerals (bottom; same symbols as in (a)).

Formation was more enriched in plagioclase relative to alkali feldspar than the Sangre de Cristo and Maroon formations.

5. Discussion

5.1. Comparison of the elemental compositions of the fine fractions and implications for provenance

In studies of moderately weathered Holocene sediment, siltstones and finer sandstones were shown to have had a more similar mineralogy and chemical

composition to the source than coarser sand fractions (Cullers, 1988, 1994a; Cullers et al., 1987, 1988). Trace element ratios such as La/Sc, Th/Sc, La/Co, and Th/Cr and the Eu anomaly size of the finer fractions were more similar to the source than the coarser sand fractions. In this study, elemental/Al₂O₂ ratios of the siltstones to fine sandstones were more similar to the shales than were those of the coarser sandstones to shales (Figs. 4 and 5). If it is assumed that some major and trace element to Al₂O₃ ratios, as well as the size of the Eu anomaly, observed in the shales to fine sandstones of each unit are the most representative to the ratios in the source, then the ratios of these fine fractions may be compared to one another to estimate composition of the provenance.

The shales to fine sandstones of the Maroon Formation have elemental concentration / Al₂O₂ ratios that are mostly the same to significantly lower than those from the Sangre de Cristo Formation (Fig. 7a). The exception is that the SiO_2/Al_2O_3 ratios are significantly higher in the Maroon Formation than in the Sangre de Cristo Formation. The main reason for these differences in these elemental ratios is probably due to the higher quartz and lower feldspar, clay minerals, and heavy minerals in the Maroon Formation relative to the Sangre de Cristo Formation. Elemental ratios of Eu/Eu*, La/Sc, Th/Sc, La/Co, Th/Co, and Th/Cr, indicative of source rock composition, are statistically the same in the Maroon and Sangre de Cristo Formations. These ratios are in the range as those derived from granitoids (Table 10). Evidently, the two formations on the average were derived from granitoids of similar composition.

The shales to fine sandstones of the Belden Formation have many elemental concentration/Al₂O₃ ratios that are statistically lower than those from the Sangre de Cristo Formation (Fig. 7b) and Maroon Formation. Only the Fe₂O₃ (total), MgO, Rb Th, Co, Sc, Cr, and Cs concentrations to Al₂O₃ ratios are statistically the same in the Belden and Sangre de Cristo Formations. Evidently, the Belden Formation contains higher quartz and calcite relative to feldspar and clay minerals. The addition of quartz and calcite diluted the concentration of many of these elements. Of the elemental ratios critical of the provenance, only the Th/Sc, La/Co, and Th/Co ratios are the same in the Belden and Sangre de Cristo fine frac-

tions. The shales to fine sandstones of the Belden Formation are significantly lower in Eu/Eu*, La/Sc, and Th/Cr ratios than those in the Sangre de Cristo Formation. These ratios for the Belden Formation are

still within the range of those derived from silicic rocks (Table 9), but it suggests a source that contains more negative Eu anomalies. Granites with larger negative Eu anomalies (low Eu/Eu*) are likely

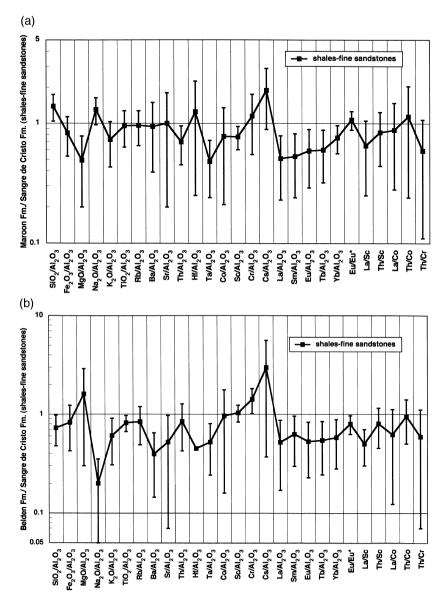


Fig. 7. (a) The elemental ratios of the average elemental concentration to Al_2O_3 of the shales to fine sandstones in the Maroon Formation are compared to those of the Sangre de Cristo Formation. Error bars represent the range of one standard deviation from the mean. (b) The elemental ratios of the average elemental concentration to Al_2O_3 of the shales to fine sandstones in the Maroon Formation are compared to those of the Belden Formation. (c) The elemental ratios of the average elemental concentration to Al_2O_3 of the medium to coarse sandstones in the Maroon Formation are compared to those of the Sangre de Cristo Formation.

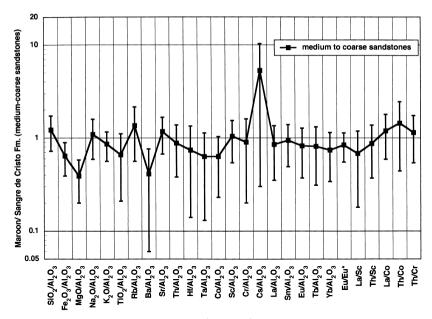


Fig. 7 (continued).

formed by more fractional crystallization of feldspar and/or by smaller degrees of melting of source rocks containing feldspar than are those with smaller negative Eu anomalies.

Table 9

The range of elemental ratios of shales to fine sandstones in this study compared to the range of ratios in similar fractions derived from granitoids and basic rocks

	Fine fractions				
	Sangre de Cristo Formation	Belden Formation	Maroon Formation	Range of sediment from silicic sources ^a	Range of sediment from basic sources ^a
Eu/Eu*	0.47-0.63	0.39-0.58	0.41-0.69	0.32-0.83	0.7-1.02
La/Sc	4.2 - 14.8	2.3-4.4	2.2 - 12.3	0.7 - 27.7	0.4 - 1.1
Th/Sc	0.71 - 14.8	0.91-1.6	0.58 - 2.0	0.64 - 18.1	0.05 - 0.4
La/Co	3.4-30	2.6 - 14.7	2.1-31.5	1.4-22.4	_
Th/Co	0.63-4.6	1.1-3.5	0.72 - 10.3	0.3 - 7.5	_
Th/Cr	0.19-0.75	0.14-0.40	0.15-0.40	0.067-4.0	0.002-0.045
	Coarse fractions				
	Sangre de Cristo Formation	Belden Formation	Maroon Formation	Range of sediment from silicic sources ^a	Range of sediment from basic sources
Eu/Eu*	0.61-0.80	_	0.36-0.69	0.40-0.94	0.71-0.95
La/Sc	4.2 - 9.5	_	2.4-4.9	2.5-16.3	0.43 - 0.86
Th/Sc	0.91 - 1.69	_	0.58 - 1.7	0.84 - 20.5	0.05 - 0.22
La/Co	6.0 - 14.2	_	4.1 - 9.7	1.8-13.8	0.14 - 0.38
Th/Co	1.2-2.3	_	0.97-3.9	0.67 - 19.4	0.04 - 1.4
	0.16-4.0		0.21-4.7	0.13-2.7	0.018 - 0.046

^aFrom Cullers, 1988, 1994a,b; Cullers and Stone, 1991; Cullers and Chaudhuri, 1993; Cullers et al., 1987, 1988.

5.2. Comparison of the composition of the medium to coarse sandstones and implications for provenance

The Belden Formation does not contain medium to coarse-grained sandstones and conglomerates, but the Sangre de Cristo and Maroon formations do contain them. Most elemental to Al₂O₂ ratios are the same in the medium to coarse sandstones of the Sangre de Cristo and Maroon Formations. The exceptions are the lower Fe₂O₃, MgO, and Ba to Al₂O₃ ratios in the Maroon than the Sangre de Cristo Formation (Fig. 7c). This suggests a lower ferromagnesian mineral amount (e.g., biotite concentrates these elements) in the Maroon relative to the Sangre de Cristo Formation perhaps due to the more intense chemical weathering in the Maroon than the Sangre de Cristo Formation. Nevertheless, the elemental ratios most diagnostic of source rock composition in the medium to coarse sandstone of these two formations (Th/Sc, La/Co, Th/Cr) do lie in the range of the ratios diagnostic of silicic source rocks as would be expected (Table 9).

5.3. Range of elemental concentrations and ratios in adjacent fine and coarse sediments and implications for metamorphic studies

Elemental concentrations relative to Al₂O₃ concentrations may differ up to a factor of 17 within the same formation although the range of most ratios is considerably less than this. It would also be of interest to see how much variation occurs in elemental concentrations and ratios in sedimentary rocks of different grain sizes in close proximity. This could potentially be helpful to interpret how much elemental variation might be expected due to sedimentary processes so that metamorphic mobility of elements in a similar suite of metasedimentary rocks could better be evaluated.

Previous studies of possible movement of elements during metamorphism have mostly made direct comparisons of individual elements rather than elemental ratios (Moss et al., 1995a,b). Thus, here mostly the elemental concentrations of coarser vs. finer fractions adjacent to one another have been compared except for a few ratios useful for provenance (Table 10).

Table 10

The range in elemental ratios of the finer fractions relative to adjacent sandstones in the formations in this study.

Element	Sangre de Cristo	Belden	Maroon
	Formation	Formation	Formation
SiO_2	0.73 - 1.11	0.71-1.26	0.68 - 1.14
Al_2O_3	0.85 - 1.34	1.48 - 3.44	0.74 - 1.42
Fe_2O_3	0.63 - 2.13	0.67 - 1.87	1.10 - 2.97
MnO	0.68 - 3.65	0.33 - 1.70	0.55 - 1.47
MgO	0.75 - 2.18	0.89 - 60.5	1.12 - 2.90
CaO	0.75 - 6.04	0.29 - 129	0.63 - 2.23
Na_2O	0.27 - 1.19	0.22 - 4.0	0.75 - 1.16
K_2O	0.82 - 1.76	1.15 - 15	0.49 - 1.45
TiO_2	0.96 - 1.33	1.51 - 3.47	0.98 - 2.20
LOI	0.78 - 4.37	0.47 - 15.0	0.62 - 2.13
Rb	0.86 - 1.64	1.55 - 8.00	0.25 - 1.48
Ba	0.41 - 1.09	0.86 - 3.92	0.88 - 7.09
Sr	0.73 - 2.55	0.60 - 3.26	0.81 - 1.80
Th	0.88 - 3.31	0.98 - 2.06	0.82 - 1.85
Hf	0.54 - 1.69	0.24 - 1.00	0.67 - 5.17
Ta	0.44 - 1.56	1.40 - 3.45	0.29 - 1.88
Co	0.73 - 4.5	0.76 - 2.14	0.90 - 4.15
Sc	0.98 - 2.09	2.18 - 6.26	0.60 - 2.06
Cr	0.78 - 2.03	1.62 - 6.71	0.77 - 3.18
Cs	0.55 - 13.0	6.4 - 22.5	0.12 - 3.60
La	0.79 - 6.3	1.33 - 3.29	0.60-1.52
Ce	0.79 - 5.8	1.40 - 2.52	0.63 - 1.47
Sm	0.92 - 5.86	1.18 - 2.93	0.76 - 1.34
Eu	0.83 - 3.65	1.18 - 1.31	1.01-1.62
Tb	0.89 - 4.17	0.65 - 1.52	1.00-1.45
Yb	0.87 - 2.34	0.77 - 1.40	1.07 - 1.73
Lu	0.81-2.16	0.79 - 1.42	1.08 - 1.59
Eu/Eu*	0.65 - 1.02	0.57 - 1.49	0.75 - 1.92
La/Sc	0.78 - 3.5	0.30 - 1.51	0.74 - 1.40
Th/Sc	0.79 - 1.76	0.21 - 0.95	0.91 - 1.43
La/Co	0.54 - 5.08	0.62 - 4.33	0.37 - 2.32
Th/Co	0.70 - 2.50	0.45 - 2.72	0.46 - 2.24
Th/Cr	0.64 - 2.78	0.19-1.28	0.36-1.14

The Belden Formation has the greatest range in the elemental concentrations between adjacent coarser and finer sediment than any of the formations (e.g., range of 0.89–60.5 of the CaO ratio of the finer to coarser fractions). The larger range in the Belden Formation is likely due to the extreme difference in the composition of the quartz-rich sandstones and the corresponding Al-rich shales.

The Maroon and Sangre de Cristo formations have more similar ranges of the elemental ratios between the finer to coarser fractions, but some elements still have fairly large variations (e.g., 0.55–13 and 0.12–3.6 range of the ratios of Cs in the

coarse to fine fractions for the Sangre de Cristo and Maroon Formations, respectively). Even ratios of elements useful for provenance determination can vary significantly between coarse and adjacent fine grained sediment (e.g., 0.54–5.08 for the range of La/Co ratios in the coarse to fine fractions in the Sangre de Cristo Formation).

Thus, large variations in absolute elemental concentration and elemental ratios characteristic of provenance occur between adjacent fine- and coarse-grained sediment in such sedimentary sequences due to sedimentary processes. Trying to unravel the movement of elements due to metamorphism over meter distances in such a heterogeneous sequence would be exceedingly difficult. The element oxide, SiO₂, has the least variation between adjacent fine- and coarse-grained sediment (32% maximum variation) so SiO₂ might potentially be the best to use for determining mobility during metamorphism. Other element oxides or elements vary by at least a factor of two between adjacent fine- and coarse-grained sediment.

Elemental variations between adjacent fine- and coarse-grained sediment of widely different mineralogical composition are intuitively likely to be larger than variations within thick sections of shale with similar mineralogical composition although evidence is not extensive for the latter. The author does have some preliminary studies within the homogeneous Graneros Shale (Colorado) that tends to support this. As seen in this study, however, it may take large scale movement of certain elements due to metamorphic processes to induce any significant variability in sediment compositions over that which occurs due to sedimentary processes within such a heterogeneous sequence.

6. Summary

(1) The quartz/feldspar ratios of the Sangre de Cristo and Maroon formations are about the same as most granitoids and are less than those observed in the Belden Formation. In addition, the alkali feldspar/plagioclase ratio increases from the Belden to the Maroon to the Sangre de Cristo Formation, but the CIW' decreases in the same order. This observation suggests a more plagioclase-rich granitoid source

and more intense weathering for the sandstones in the Belden Formation than in the Maroon and Sangre de Cristo formations.

- (2) Many of the elemental concentration/Al₂O₃ ratios of the medium-coarse sandstones relative to shales are significantly different than those of the fine-medium sandstones relative to shales of the Sangre de Cristo Formation. Also, many of the elemental/Al₂O₃ ratios of the fine-medium sandstones relative to shales of the Maroon Formation are significantly different. The Belden Formation has larger differences in the elemental concentration/Al₂O₃ ratios in all sediment than does sediment from the Sangre de Cristo and Maroon Formations. Nevertheless, most elemental concentration/Al₂O₃ ratios of shales and siltstones of the Belden Formation are statistically the same as those of the sandstones.
- (3) Variation in the elemental composition of the samples may be explained by the observed variation in mineralogy of the samples. For example, high SiO₂/Al₂O₃ ratios of the Belden sandstones are due to enrichment in quartz relative to other minerals; the low SiO₂/Al₂O₃ ratios of the Belden shales are due to enriched Al-rich clay minerals relative to quartz. Also the covariation in SiO₂ and Al₂O₃ within the Belden shales suggests that Al- and Si-poor minerals like opaque minerals and calcite are causing varied dilution of SiO₂ and Al₂O₃.
- (4) Most ratios of elemental concentration/Al₂O₃ of the shales-siltstones are statistically the same in the Maroon and Sangre de Cristo formations. Elemental ratios indicative of provenance are also the same in the Maroon and Sangre de Cristo formations and are in the range of those derived from granitoids. The shales-fine sandstones of the Belden Formation have many elemental ratios that are statistically lower than those of the Maroon and Sangre de Cristo Formations (e.g., Eu/Eu*, La/Sc, and Th/Cr ratios). This suggests that the Belden Formation was derived from a granitoid source formed by more fractional crystallization of feldspar or a lesser degree of melting from a feldspar-rich source than the granitoids that weathered to produce the Maroon and Sangre de Cristo Formations.
- (5) The variation in the elemental concentrations or ratios between adjacent fine and coarse-grained sediment is large over less than 1 m distances (factors of 0.2 to 60). This suggests that studies of

elemental mobility due to metamorphism in sequences like this would be useless unless variation in elemental composition due to metamorphism was much larger than this.

Acknowledgements

I thank the crew of the nuclear reactor at Kansas State University for irradiating these samples and the Department of Nuclear Engineering for the use of their equipment. Also, Cecile Stephens is thanked for the analytical assistance.

References

- Bolyard, D.W., 1959. Pennsylvanian and Permian stratigraphy in the Sangre de Cristo Mountains between La Veta Pass and Westcliffe, Colorado, Am. Assoc. Pet. Geol. 43, 1896–1939.
- Brill, K.G.J., 1952. Stratigraphy in the Permo-Pennsylvanian zeugogeosyncline of Colorado and northern New Mexico. Bull. Geol. Soc. Am. 63, 809–880.
- Cardenas, A.A. et al., 1996. Assessing differences in composition between low metamorphic grade mudstones and high-grade schists using log ratio techniques. J. Geol. 104, 279–293.
- Chittleborough, D.J., 1991. Indices of weathering for soils and palaeosols formed on silicate rocks. Aust. J. Earth Sci. 38, 115–120.
- Condie, K.C., 1991. Another look at rare earth elements in shales. Geochim. Cosmochim. Acta 55, 2527–2531.
- Condie, K.C., Dengate, J., Cullers, R.L., 1995. Behavior of rare earth elements in a paleoweathering profile on granodiorite in the Front Range, Colorado, USA. Geochim. Cosmochim. Acta 59, 279–294.
- Condie, K.C., Wronkiewicz, D.J., 1990. The Cr/Th ratio in Precambrian pelites from the Kaapvaal craton as an index of craton evolution. Earth Planet. Sci. Lett. 97, 256–267.
- Cox, R., Low, D.R., Cullers, R.L., 1995. The influence of sediment recycling and basement composition on evolution of mudrock chemistry in the southwestern United States. Geochim. Cosmochim. Acta 59, 2919–2940.
- Cullers, R.L., 1988. Mineralogical and chemical changes of soil and stream sediment formed by intense weathering of the Danberg granite, Georgia, USA, Lithos 21, 301–314.
- Cullers, R.L., 1994a. The chemical signature of source rocks in size fractions of Holocene stream sediment derived from metamorphic rocks in the Wet Mountains region, USA. Chem. Geol. 113, 327–343.
- Cullers, R.L., 1994b. The controls on the major and trace element variation of shales, siltstones, and sandstones of Pennsylvanian-Permian age from uplifted continental blocks in Colorado to platform sediment in Kansas, USA. Geochim. Cosmochim. Acta 58, 4955-4972.

- Cullers, R.L., Barrett, T., Carlson, R., Robinson, B., 1987. Rare-earth element and mineralogic changes in Holocene soil and stream sediment: a case study in the Wet Mountains, Colorado, USA. Chem. Geol. 63, 275–297.
- Cullers, R.L., Basu, A., Suttner, L., 1988. Geochemical signature of provenance in sand-size material in soils and stream sediments near the Tobacco Root batholith, Montana, USA. Chem. Geol. 70, 335–348.
- Cullers, R.L., Berendsen, P., 1998. The provenance and chemical variation of sandstones associated with the Mid-continent rift system, USA. European Journal of Mineralogy 10, 987–1002.
- Cullers, R.L., Ramakrishnan, S., Berendsen, P., Griffin, T., 1985. Geochemistry and petrogenesis of lamproites, Late Cretaceous age, Woodson, Kansas, USA. Geochim. Cosmochim. Acta 49, 1383–1402.
- Cullers, R.L., Stone, J., 1991. Chemical and mineralogical comparison of the Pennsylvanian Fountain Formation, Colorado, USA (an uplifted continental block) to sedimentary rocks from other tectonic environments. Lithos 27, 115–131.
- De Voto, R.H., 1972. Pennsylvanian and Permian stratigraphy and tectonism in central Colorado. Colorado School of Mines Ouarterly 67 (4), 139–185.
- De Voto, R.H., 1980. Pennsylvanian stratigraphy and history of Colorado. In: Kent, H.C., Porter, K.W. (Eds.), Colorado Geology. Rocky Mountain Assoc. of Geologists, Denver, CO, pp. 71–101.
- Flores, R.J., 1984. Sedimentation model for the Crestone Conglomerate Member of the Sangre de Cristo Formation (Pennsylvanian–Permian), South-central Colorado. MA Thesis, Indiana University, Bloomington, IN, 132 pp.
- Fyffe, L.R., Pickerill, R.K., 1993. Geochemistry of Upper Cambrian-Lower Ordovician black shale along a northeastern Appalachian transect. Geol. Soc. Am. Bull. 105, 897-910.
- Girty, G.H., Hanson, A.D., Yoshinobu, A.S., Knaack, C., Johnson, D., 1993. Provenance of Paleozoic mudstones in a contact metamorphic aureole determined by rare earth element, Th, and Sc analyses, Sierra Nevada, California. Geology 21, 363–366.
- Girty, G.H., Ridge, D.L., Knaack, C., Johnson, D., Al-Riyami, R.K., 1996. Provenance and depositional setting of Paleozoic chert and argillite, Sierra Nevada, California. J. Sediment. Res. 66, 107–118.
- Gordon, G.E. et al., 1968. Instrumental neutron activation analysis of standard rocks with high resolution gamma-ray detectors. Geochim. Cosmochim. Acta 32, 369–396.
- Gouveia, M.A. et al., 1993. Behavior of REE and other trace and major elements during weathering of granitic rocks, Évora, Portugal. Chem. Geol. 107, 293–296.
- Harnois, L., 1988. The CIW index: a new chemical index of weathering. Sedimentary Geology 55, 319–322.
- Jacobs, J.W., Korotov, R.L., Blanchard, D.P., Haskin, L.A., 1977.
 A well-tested procedure for instrumental neutron activation analysis of silicate rocks and minerals. J. Radioanal. Chem. 40, 93–114.
- Johnson, S.Y., 1987. Sedimentology and paleogeographic significance of six fluvial sandstone bodies in the Maroon Formation, Eagle Basin, Northwest Colorado. Evolution of sedimen-

- tary basins Uinta and Peceance Basins. US Geological Survey, pp. 1–18.
- Lindsey, D.A., Clark, R.F., Soulliere, S.J., 1987. Minturn and Sangre de Cristo Formations of Southern Colorado: a prograding fan delta and alluvial fan sequence shed from the Ancestral Rocky Mountains. In: Peterson, J.A. (Ed.), Paleotectonics and Sedimentation in the Rocky Mountain Region, United States. The American Assoc. of Petroleum Geologists, Tulsa, OK, pp. 541–561.
- Maughin, E.K., 1980. Pennsylvanian stratigraphy and history of Colorado. In: Kent, H.C., Porter, K.W. (Eds.), Colorado Geology. Rocky Mountain Assoc. of Geologists, Denver, CO, pp. 103–110.
- McLennan, S.M., Taylor, S.R., Eriksson, K.A., 1983. Geochemistry of Archean shales from the Pilbara Supergroup, Western Australia. Geochim. Cosmochim. Acta 47, 1211–1222.
- McLennan, S.M., Taylor, S.R., McCulloch, M.T., Maynard, J.B., 1990. Geochemistry and Nd–Sr isotopic composition of deepsea turbidites: crustal evolution and plate tectonic associations. Geochim. Cosmochim. Acta 54, 2014–2050.
- McLennan, S.M., Hemming, S., McDaniel, D.K., Hanson, G.N., 1993. Geochemical approaches to sedimentation, provenance, and tectonics. In: Johnson, M.J., Basu, A. (Eds.), Processes Controlling the Composition of Clastic Sediments. Geological Society of America, Boulder, CO, pp. 21–40.
- Medlin, J.H., Suhr, N.H., Bodkin, J.R., 1969. Atomic absorption analysis of silicates employing lithium metaborate fusion. At. Absorpt. Newsl. 8, 25–29.
- Moss, B.E., Haskin, L.A., Dymek, R.F., 1995a. Compositional variations in metamorphosed sediments of the Littleton and Carrabassett Formations, New Hampshire at sub-hand specimen, outcrop, and regional scales.
- Moss, B.E., Haskin, L.A., Dymek, R.F., Shaw, D.M., 1995b. Redetermination and reevaluation of compositional variations in metamorphosed sediments of the Littleton Formation, New Hampshire. Am. J. Sci. 295, 988–1019.
- Moss, B.E., Haskin, L.A., Dymek, R.F., 1996. Compositional variations in metamorphosed sediments of the Littleton Formation, New Hampshire, and the Carrabassett Formation, Maine,

- at sub-hand specimen, outcrop, and regional scales. Am. J. Sci. 296 473-493
- Murray, R.W., Bucholtz Ten Brink, M.R., Gerlach, D.C., Russ, G.P.I., Jones, D.L., 1991. Rare earth, major, and trace elements in chert from the Franciscan Complex and Monterey Group, California: assessing REE sources in fine-grained marine sediments. Geochim. Cosmochim. Acta 52, 1875–1895.
- Nesbitt, H.W., 1979. Mobility and fractionation of rare earth elements during weathering of a granodiorite. Nature 279, 206–210
- Nesbitt, H.W., Markovics, G., 1997. Weathering of granodioritic crust, long-term storage of elements in weathering profiles, and petrogenesis of siliciclastic sediments. Geochim. Cosmochim. Acta 61, 1653–1670.
- Nesbitt, H.W., Young, G.M., 1982. Early Proterozoic climates and plate motions inferred from major elemental chemistry of lutites. Nature 199, 715–717.
- Nuccio, V.F., Schenk, C.J., 1987. Burial reconstruction of the Early and Middle Pennsylvanian Belden Formation, Gilman area, Eagle Basin, northwest Colorado. Evolution of sedimentary basins — Uinta and Piceance basins. US Geol. Survey, pp. 31–36.
- Shapiro, L., 1978. Rapid analysis of silicate, carbonate, and phosphate rocks-revised edition, 1401. US Geol. Sur. Bull.
- Suttner, L.J., Dutta, P.K., 1986. Alluvial sandstone composition and paleoclimate: I. Framework mineralogy. J. Sediment. Petrol. 56, 329–345.
- Tweto, O., Lovering, T.S., 1977. Geology of the Minturn 15-minute Quadrangle. Eagle and Summit Counties, Colorado. Geological Survey Prof. Paper, 956. US Geological Survey, Washington, DC, 57 pp.
- Ugidos, J.M. et al., 1997. Provenance of Upper Precambrian— Lower Cambrian shales in the Central Iberian Zone, Spain: evidence from a chemical and isotopic study. Chem. Geol. 136, 55–70.
- Wronkiewicz, D.J., Condie, K.C., 1990. Geochemistry and mineralogy of sediments from the Ventersdorp and Transvaal Supergroups, South Africa: cratonic evolution during the early Proterozoic. Geochim. Cosmochim. Acta 54, 343–354.