



## The influence of sediment recycling and basement composition on evolution of mudrock chemistry in the southwestern United States

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**Abstract**—This paper reports systematic changes in mudrock composition through time on a single continental crustal block. The changes reflect both sediment recycling processes and changes through time in the composition of crystalline material being added to the sedimentary system and are related to tectonic evolution as the block matures from a series of accreted arc terranes to a stable craton.

The major and trace element distributions reflect different aspects of the provenance of the mudrocks in this study. Major elements record sediment recycling processes as well as changing proportions of sedimentary and first-cycle source rocks. With the exceptions of K<sub>2</sub>O (which tends to increase), and SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> (which show no trend), most major oxides tend to decline in relative abundance in younger mudrocks. Patterns shown by the Index of Compositional Variability ( $[(Fe_2O_3 + K_2O + Na_2O + CaO + MgO + MnO + TiO_2)/Al_2O_3]$ ) and by K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> indicate that the major oxide trends are due to decreasing proportions of nonclay silicate minerals and a concomitant increase in the proportion of clay minerals, probably due to decreasing input of first cycle detritus coupled with recycling of sedimentary material. Excursions from progressive trends, marked by increases in MgO, K<sub>2</sub>O, and CaO, reflect episodes of large-scale input of nonclay first-cycle minerals from crystalline source rocks due to large-scale basement uplift.

The chemistry of low-solubility trace elements, in contrast, is not sensitive to recycling effects and reflects the composition of first-cycle input. Incompatible elements are progressively enriched relative to compatible elements in younger mudrocks, and values for chondrite normalised rare earth elements also increase. In addition, the Eu anomaly becomes systematically more negative in younger samples. These trends cannot be explained by diagenetic or weathering processes, and, therefore, indicate that the proportion of fractionated granitic first-cycle detritus being added to the sedimentary system becomes greater with time.

These results confirm the importance of tectonic setting in controlling mudrock chemistry, and also demonstrate that there is a dynamic relationship between the tectonic evolution of a continental block and the composition of its sedimentary mantle.

### 1. INTRODUCTION

The generalisation is frequently made that mudrocks represent samples of the average continental crust (e.g., Allègre and Rousseau, 1984; Taylor and McLennan, 1985), which is certainly true of muds from the ocean basins, the constituents of which have been transported long distances and thoroughly mixed. Most mudrocks, however, form in more confined basins and from more restricted source rocks and are not globally homogenised: Bhatia and Taylor (1981) and Bhatia (1985) have shown that the compositions of mudrocks from volcanic arc settings are related to the compositions of their source rocks, and bear little resemblance to average shale compositions.

In studies of global variation in mudrock chemistry (Garrels and Mackenzie, 1971; Ronov and Migdisov, 1971; Taylor and McLennan, 1985), the average mudrock composition for any given time interval is typically computed from a collection of individual mudrock samples, each of which was derived from specific source rock types in specific tectonic set-

tings. Information about the controls on mudrock composition on a local scale is, therefore, critical to an understanding of variations in mudrock composition on a global scale. However, with the exception of the work of Bhatia and co-workers (Bhatia and Taylor, 1981; Bhatia, 1983; Bhatia and Crook, 1986), which focuses largely on sediments in volcanic arc settings, and that of van de Kamp on the Pacific margin of North America (van de Kamp et al., 1976; van de Kamp and Leake, 1985), little information is available on the effects of provenance and tectonic setting on the composition of mudrocks.

The aim of this paper is to investigate secular changes in mudrock composition on a single crustal block, which we define as a piece of continental crust with a restricted crystallisation or accretion age, distinct from that of the crustal blocks around it. We report on the compositions of mudrocks deposited on the Colorado Province during the time interval 1.8–0.2 Ga. This time interval spans the time of formation of the crustal material, its cratonisation period, and its subsequent stable cratonic history. The specific objectives of this paper are (a) to establish whether time-related changes in chemistry can be identified in a series of mudrocks deposited

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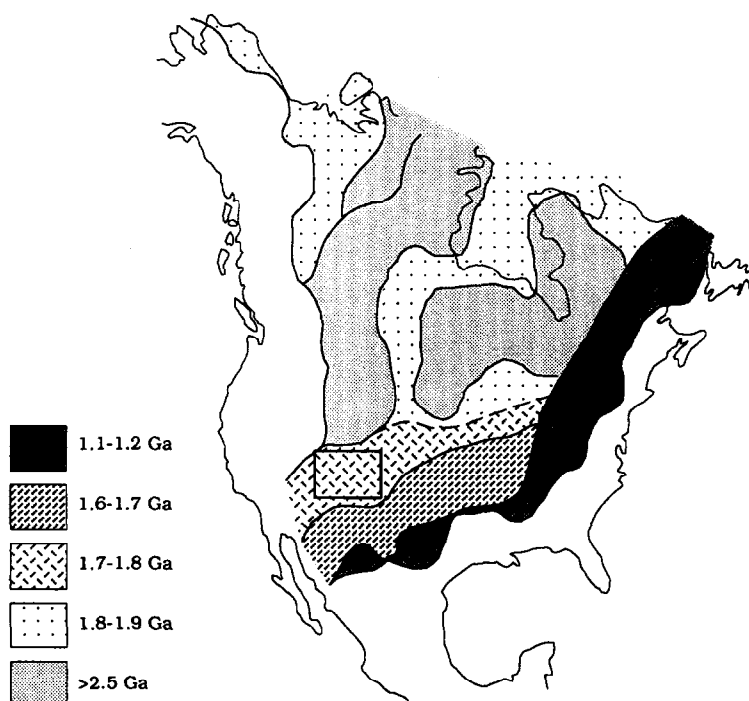


FIG. 1. Distribution of Precambrian age provinces in North America (after Karlstrom et al., 1987). The Colorado Province has a crystallisation age of about 1.8–1.7 Ga. The box shows the approximate limits of the study area.

on a crustal block as it evolves into a mature craton, and (b) to investigate the relative importance of sediment recycling and first-cycle input in governing mudrock chemistry on a regional scale over time.

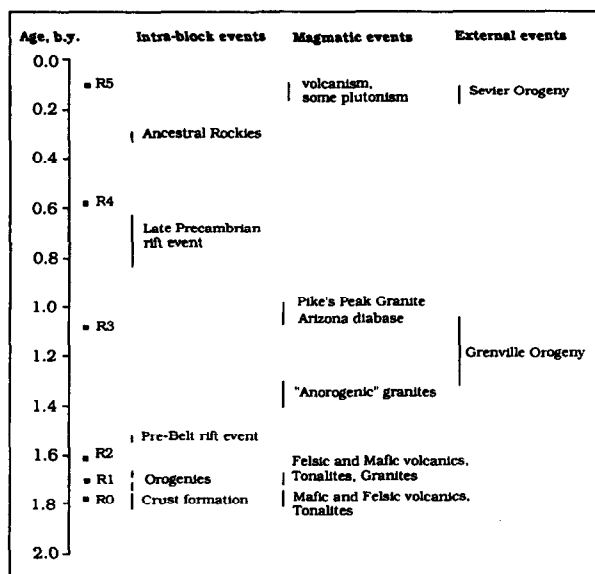


FIG. 2. Distribution of ages of sedimentary sequences in each sedimentation interval and of major tectonic events that affected the Colorado Province, both directly (intra-block events) and indirectly (external events). Ages are taken from compilations in Kauffman (1977), Elston (1989), Hoffman (1989), Cox et al. (1991), and Karlstrom and Bowring (1991).

## 2. STUDY AREA: THE COLORADO PROVINCE

### 2.1. Crust Formation and Orogenic History

The Colorado Province (Bickford et al., 1986) is the basement complex that underlies much of the southwestern U.S. (Fig. 1). The oldest rocks in the Colorado Province are metamorphosed and strongly deformed Early Proterozoic volcanic units and immature volcanic sediments (Condie and Neuter, 1981; Condie, 1982; Bickford and Boardman, 1984; Boardman, 1986a,b). The mafic volcanic sequences are dated to about 1.80–1.70 Ga and are associated with 1.79–1.74 Ga calc-alkalic intrusive rocks and felsic volcanic rocks (Silver and Barker, 1967; Anderson et al., 1971; Reed et al., 1987; Van Schmus et al., 1987). The province probably formed by the accretion of several arc-related terranes onto the southern edge of the Archean North American craton (Condie and Neuter, 1981; Bickford and Boardman, 1984; Condie, 1986; Karlstrom et al., 1987; Silver, 1987; Karlstrom and Bowring, 1988, 1992; Van Schmus et al., 1992). The chemistry of the volcanic rocks indicates that they represent both evolved oceanic and continental margin arcs (Condie, 1986). Orogenic events accompanying accretion occurred during the approximate intervals 1.70–1.75 and 1.65–1.60 Ga (Karlstrom and Bowring, 1988; Bowring and Karlstrom, 1990; Karlstrom and Bowring, 1991) (Fig. 2). Subsequent post-cratonisation deformation of the Colorado Province was dominated by vertical movements, regional upwarping, and extensional block faulting (Grose, 1972; Mallory, 1972; King, 1977; Keith and Wilt, 1986; Baars et al., 1988; Sloss, 1988), with little or no metamorphism and limited involvement of basement.

### 2.2. Magmatic History

Magmatism during the time interval of interest may be assigned to three main phases: (a) magmatism accompanying accretion and early orogeny; (b) 1.4 Ga anorogenic magmatism; and (c) 1.0 Ga Grenvillian magmatism.

(a) Magmatism associated with the early history of the Colorado Province includes early, arc-related volcanism, generally consisting

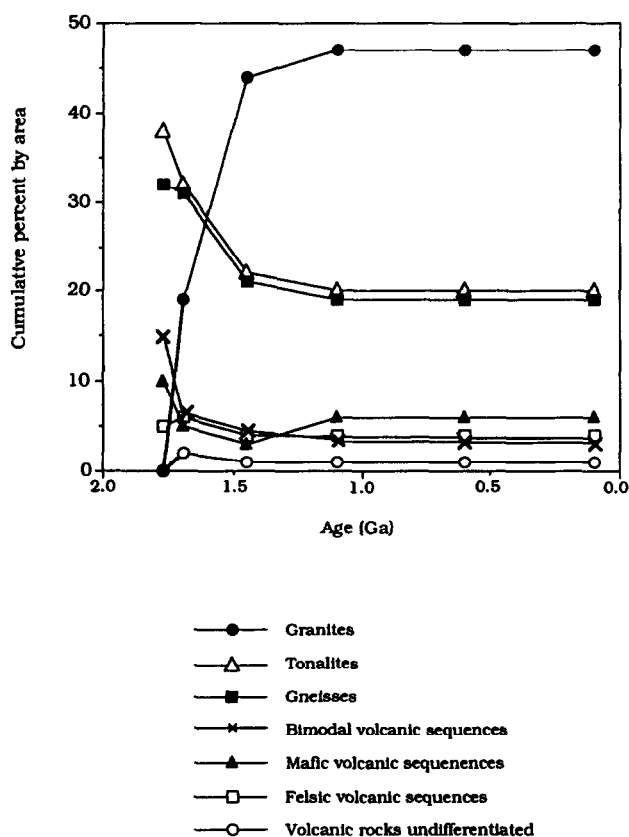


FIG. 3. Distribution through time of rock types in the basement of the Colorado Province. The values are based on present-day areal exposure of rock types of different ages (Shride, 1967; Condie, 1981), and so represent only a crude estimate of the actual distribution of crystalline source rocks in the past, but the increasing dominance of granitic material is evident.

of bimodal basalt-dacite-rhyolite assemblages. These volcanic rocks and younger supracrustal sequences are intruded by tonalites and monzonites and occasional gabbros (Bickford and Boardman, 1984; Boardman, 1986b; Condie, 1986; Reed et al., 1987; Bickford, 1988).

(b) A suite of subalkalic and peraluminous granites with ages ranging from 1.46–1.36 Ga intrudes the Colorado Province basement (Anderson, 1983). These are broadly coeval with, and probably genetically related to, the igneous rocks of the Granite-Rhyolite Provinces of the mid-Continent, as described by Bickford et al. (1986) and Van Schmus et al. (1987).

(c) The latest magmatic event of consequence on the Colorado Province during the interval of interest is represented by the 1.02 Ga Pikes Peak Batholith, which consists of granite with minor associated syenites and gabbros (Barker et al., 1975; Tweto, 1987), and by volumetrically minor 1.1 Ga mafic dykes and lavas in the Apache Group and Grand Canyon Supergroup (Condie, 1981; Elston, 1989; Wrucke, 1989).

Figure 3 shows the proportions of mafic and granitic basement rock in the Colorado Province as a function of age. Early, accretion-related magmatism included a high proportion of mafic material, but later additions to the upper crust have consisted primarily of granitic plutons, with rare and volumetrically minor events of mafic volcanism (Anderson, 1989b; Bickford et al., 1989; Hoffman, 1989).

### 2.3. Basin-Forming Events and Sedimentation History

The tectonic setting of the Colorado Province has changed through time as it has evolved from a series of arc complexes into a mature

craton. The oldest sediments consist of immature, volcanic-arc derived detritus; the latest ones studied are the supermature deposits of the Dakota Sandstone. The intervening sequences consist of sediments at varying stages of maturity. The sequences examined in the course of this project represent the 1.7–1.8 Ga arc-related rocks, designated R0, and five subsequent sedimentation and recycling intervals, designated R1 to R5 (Fig. 2).

The Colorado Province basement (R0) consists of arc-related volcanic rocks, generally bimodal in composition, which have been deformed, intruded by several generations of plutonic rocks, and metamorphosed to upper greenschist or lower amphibolite facies (Bickford, 1988; Grambling et al., 1989; Williams, 1991). The Ash Creek Group and the Yavapai Supergroup in Arizona were sampled.

Subsequent sedimentation and recycling intervals (R1–R5) mark times during which there were both regional exposure of sedimentary rocks and widespread deposition of shallow marine sediment. The sedimentary sequences deposited during these sedimentation intervals range in age from about 1.7 to 0.2 Ga (Fig. 2). The provenance and tectonic setting of each of these sequences is described in detail in Cox and Lowe (1995b).

R1 sequences include the Vallecito Formation (Colorado), the Alder Group and Texas Gulch Formation (Arizona), and the Vadito Group (New Mexico). These sediments were deposited in settings related to the accreting arc complexes, and on a shallow shelf which developed on top of the older volcanic arc (Soegaard and Eriksson, 1986; Gonzales, 1988; Reed, 1988; Mawer et al., 1990; Condie et al., 1992). They were derived largely by erosion of pencontemporaneous felsic and mafic volcanogenic rocks (Gastil, 1958; Reed, 1988; Mawer et al., 1990).

R2 sequences include the Hondo Group (New Mexico), the Matatzal Group and Hess Canyon Group (Arizona), and the Uncompaghe Formation (Colorado). These sediments were probably deposited in local, fault bounded basins which formed during the Yavapai Orogeny (Bayne, 1987; Bowring and Karlstrom, 1990). They were derived from the volcanic arc successions and metamorphic rocks of the recently uplifted orogen and contemporaneous rhyolitic volcanic rocks (Trevena, 1979; Bayne, 1987; Harris and Eriksson, 1987; Neet and Knauth, 1989; Doe and Karlstrom, 1991).

R3 sequences are limited to the Grand Canyon Supergroup and Apache Group (Arizona). These sediments were deposited in fault-bounded intracratonic basins which formed in the latter part of the Proterozoic, approximately between 1.3–0.8 Ga (Elston, 1989), and have been interpreted to represent widespread extension and attempted rifting of the North American continent (Stewart and Poole, 1974; Stewart, 1978, 1982; Wrucke, 1989). Source rocks for the sediments included the contemporaneous mafic igneous rocks and the newly-exposed 1.4 Ga granites, along with the sedimentary and metamorphic rocks of R2, R1, and R0 (Middleton and Trujillo, 1984; Wrucke, 1989; Cox and Lowe 1995b).

R4 sequences are represented by the Tapeats Sandstone and Bright Angel Shale (Arizona) and Ignatio Quartzite (Colorado). They record transgressive deposition across the newly-formed western margin of the North American craton (Lochman-Balk, 1971, 1972; Stewart, 1972, 1982). The sediments were derived from sedimentary and metamorphic rocks representing the intervals R0–R3 and from 1.4 Ga granites.

R5 sediments of the Dakota Sandstone, Mancos Shale, and correlative equivalents (Arizona, New Mexico, Colorado and Utah) were deposited in the Cretaceous Interior Seaway, which developed in response to uplift of the Sevier foreland fold and thrust belt (Schwans, 1988; Weiss and Roche, 1988). They are Upper Cretaceous sediments (Curtis, 1988; Molenaar, 1988; Peterson, 1988), derived from uplifted Late Precambrian and Paleozoic marginal sequences and Mesozoic continental sequences in the thrust belt (Mackenzie and Poole, 1962; Bauer, 1989).

## 3. METHODS

### 3.1. Sampling Technique

Mudrock samples were collected throughout the Colorado Province (Fig. 4). The precise localities are given in Cox (1993). All

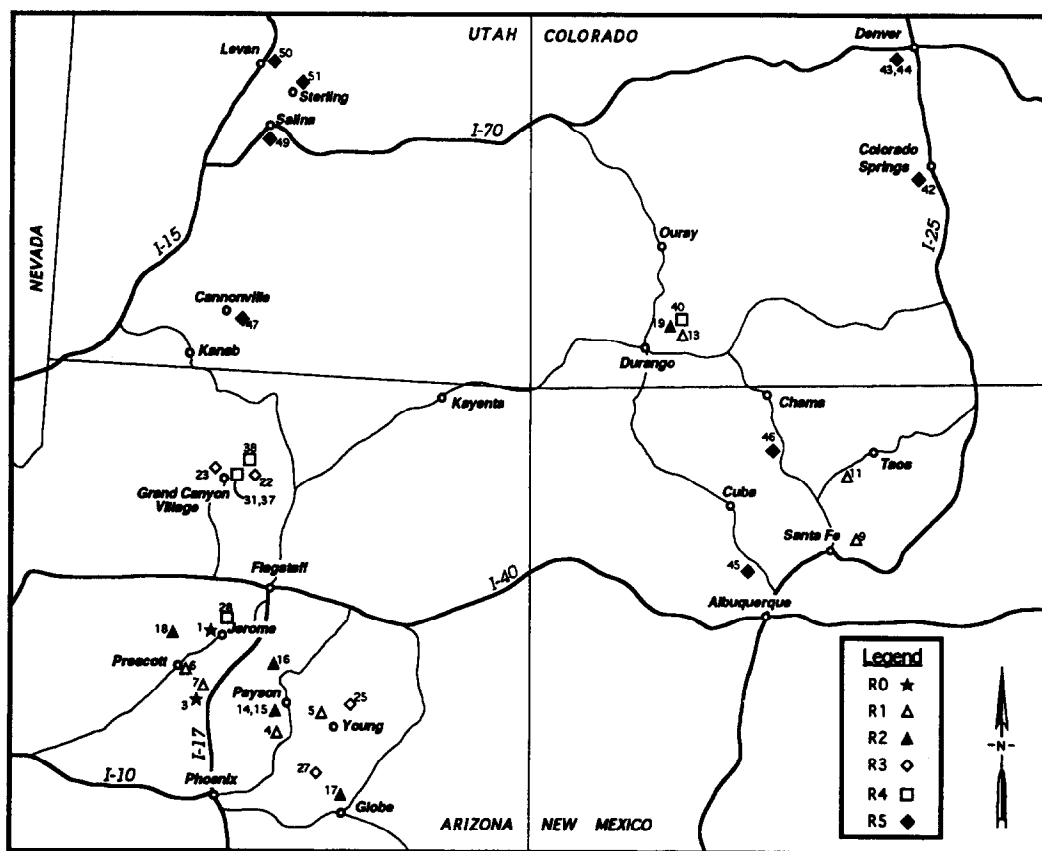


FIG. 4. Location map showing study area and sample sites. Details of sample localities are given in Cox (1993).

were associated with sands deposited in shallow or marginal marine settings (Cox, 1993; Cox and Lowe, 1995b). Shallow marine depositional environments cover broad areas and receive sediment from many streams and by aeolian transport. The sediment is transported and mixed within the marine setting by currents and by waves, so that the final deposit represents an average of detritus from many sources. Sampling sequences from a specific depositional environment also permits comparison between sample localities and between sedimentation intervals without the need to compensate for compositional and textural effects which might be a function of depositional setting.

### 3.2. Analytical Techniques

Major element analyses were performed by Ron Hartree at the University of Ottawa. Samples were prepared as fused disks, using a mixture of 0.43 g  $\text{Li}_2\text{CO}_3$ , 3.9 g  $\text{Li}_3\text{BO}_4$ , and 1.3 g sample (R. Hartree, pers. commun.). The samples were analysed on a Phillips PW 1410/80 X-ray fluorescence spectrometer, using matrix correction coefficients given in de Jongh (1973) and Rousseau (1984a,b). Total Fe content is reported as  $\text{Fe}_2\text{O}_{3(\text{t})}$ . Average analyses for USGS standards run concurrently with the study samples are given in Table 1a.

Trace element analyses (Zr, Y, Sr, U, Pb, Ga, Zn, Cu, Ni, Ti, and V) were obtained at Stanford University on a Rigaku S-max automated X-ray fluorescence spectrometer with a rhodium X-ray source. Sample preparation and analysis followed methods described in Norrish and Chappell (1977). Mass absorption coefficients were calculated according to Reynolds (1963, 1967) and Walker (1973). Av-

erage analyses for concurrently run USGS standards are presented in Table 1b.

The concentrations of seven rare earth elements (La, Ce, Sm, Eu, Tb, Yb, and Lu) and of the trace elements Rb, Ba, Th, Hf, Sc, and Cr were determined by instrumental neutron activation at Kansas State University after methods given in Gordon et al. (1968) and Jacobs et al. (1977) (Cullers et al., 1988). Compositions of standard rocks analysed using these techniques are reported in Cullers et al. (1979, 1987). Standard errors are tabulated in Cox et al. (1991).

The REE chondrite normalisation factors used in this study are those of Wakita et al. (1971). Alternative normalisation factors (Evensen et al., 1978) have been used in other studies (e.g., Taylor and McLennan, 1985). There is little difference between the REE patterns produced: normalising to Evensen et al. (1978) shifts the patterns to slightly lower values of sample/chondrite.

### 3.3. Statistical Methods

For brevity, the statistics presented in this paper are limited to trend analysis and estimates of error on group averages; for a more extensive statistical treatment of the results see Cox (1993). The median is used as the summary statistic because it provides a robust estimate of central tendency for datasets drawn from a population whose distribution pattern is unknown, and for which a normal distribution cannot be assumed (Lister, 1982; Rock et al., 1987; Rock, 1988). The confidence level on the error bars (shown in Figs. 7, 8, 9, 12) varies from 94% to 98% (see Lister 1982; Appendix III). The errors were calculated using methods based on the binomial distribution, as described in Daniel (1990). Geologic discus-

Table 1. Average analyses for standard rocks used during this study. Published values are from Govindaraju (1989).

## a. Major elements, wt. %

	BHVO-1 Published value	This study, average of 5	*S.D.	DR-N Published value	This study, average of 18	S.D.	SY-2 Published value	This study, average of 10	S.D.	G2 Published value	This study, average of 8	S.D.
SiO <sub>2</sub>	49.94	49.71	0.20	52.85	53.04	0.19	60.05	60.06	0.11	69.08	69.05	0.32
Al <sub>2</sub> O <sub>3</sub>	13.80	13.66	0.06	17.52	17.67	0.12	12.04	12.10	0.06	15.38	15.31	0.10
Fe <sub>2</sub> O <sub>3</sub> (t)	12.23	12.37	0.06	9.70	9.70	0.10	6.31	6.28	0.08	2.66	2.74	0.02
MgO	7.23	7.36	0.04	4.40	4.34	0.05	2.69	2.66	0.02	0.75	0.66	0.04
CaO	11.40	11.41	0.03	7.05	7.00	0.03	7.98	7.99	0.02	1.96	1.93	0.01
Na <sub>2</sub> O	2.26	2.10	0.16	2.99	2.90	0.14	4.31	4.50	0.13	4.08	4.24	0.13
K <sub>2</sub> O	0.52	0.52	0.00	1.70	1.70	0.01	4.44	4.48	0.02	4.48	4.48	0.02
TiO <sub>2</sub>	2.71	2.72	0.01	1.09	1.05	0.01	0.14	0.13	0.00	0.48	0.48	0.00
P <sub>2</sub> O <sub>5</sub>	0.27	0.26	0.01	0.25	0.22	0.01	0.43	0.44	0.01	0.14	0.13	0.01
S	0.01	0.01	0.00	0.04	0.02	0.00	0.02	0.03	0.00	0.01	0.00	0.00
MnO	0.17	0.17	0.00	0.22	0.22	0.00	0.32	0.33	0.00	0.03	0.04	0.00

## b. Trace elements, ppm

	AGV-1 Published value	This study, average of 21	*S.D.	BHVO-1 Published value	This study, average of 24	S.D.	G2 Published value	This study, average of 12	S.D.
Nb	15.00	14.56	0.26	19.00	18.55	0.42	12.00	12.20	0.12
Zr	227.00	243.77	1.77	179.00	178.29	1.20	309.00	326.14	2.64
Y	20.00	19.10	0.38	27.60	25.52	0.45	11.00	9.73	0.53
Sr	662.00	665.09	4.36	403.00	390.54	2.17	478.00	481.57	3.10
U	1.92	2.96	0.53	0.42	1.20	0.74	2.07	2.46	0.51
Pb	36.00	36.81	1.44	2.60	7.08	0.95	30.00	31.86	1.11
Ga	20.00	19.96	0.47	21.00	21.09	0.73	23.00	21.76	0.33
Zn	88.00	89.67	1.05	105.00	108.88	1.26	86.00	86.89	0.56
Cu	60.00	62.63	1.73	136.00	137.06	2.02	11.00	10.46	0.66
Ni	16.00	14.60	0.83	121.00	117.81	1.05	5.00	5.22	0.62
TiO <sub>2</sub> %	1.05	1.05	0.01	2.71	2.75	0.02	0.48	0.47	0.00
V	121.00	121.93	3.56	317.00	315.31	6.38	36.00	37.29	2.29

\*S.D.= one standard deviation about the average

sion of this methodology may be found in Lister (1982), Rock et al. (1987), and Rock (1988).

In fact, analysis of these data has shown that the mean and the median for each sedimentation interval are the same within error (Cox, 1993). Therefore, the data are by definition normally distributed. For this reason, the analysis of trends is based on standard linear regression. The p value shown (Figs. 7, 8, 9, 11, 12) is the computed probability that the slope of the regression line is not zero. Values less than 0.0500 indicate that trends are significant above the .95 level; values less than 0.0100 indicate that trends are significant above the .99 level.

#### 4. BULK ROCK CHEMISTRY AS AN INDEX OF MUDROCK COMPOSITION

Chemistry is the best index of compositional difference between mudrocks of different age, provenance, and diagenetic history. Because clay minerals are labile and recrystallise readily, radical mineralogical changes occur during diagenesis and low-grade metamorphism (Burst, 1959; Weaver, 1967a,b; Dunoyer de Segonzac, 1970; Weaver and Beck, 1971; Hower et al., 1976; Sudo, 1978; Eslinger and Sellars, 1981; Weaver, 1989). These processes are largely isochemical: some local redistribution of material may occur, but large-scale dispersal or addition of components is uncommon

(Haskin et al., 1968; Weaver and Beck, 1971; Cullers et al., 1974; Hower et al., 1976; Ronov et al., 1977; Hower, 1981; Rösler and Beuge, 1983; Bau, 1991). Therefore, although mudrock mineralogy may differ from that of the deposited sediment, the bulk composition remains largely the same.

The patterns seen in the major element chemistry of the Colorado Province mudrocks reflect changes through time in the mineralogy of fine-grained detritus entering the sedimentary system; but the present-day mineralogy of the Colorado Province mudrocks is related to their diagenetic history, and can be expected to vary as a function of age and degree of recrystallisation. The rocks studied have experienced differing degrees of diagenesis, and the oldest sequences have undergone metamorphism (Nielsen and Scott, 1979; Soegaard and Eriksson, 1985; Harris, 1990; Gillentine et al., 1991). Consequently, chemical composition and oxide ratios are used in this discussion as indicators of original detrital mineralogy to permit direct comparisons between samples of different ages.

Oxide ratios can be used to characterise differences between samples. Clay minerals and nonclay silicate minerals are characterised by very different proportions of alumina.

Table 2. Major element concentrations in weight % for mudrocks of the basement (R0) and 5 sediment recycling intervals (R1 - R5).

Sequence	Sample	R	Loc. †	LOI	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub> *	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	Total
Ash Creek	AC.J.139.1	0	1	1.54	74.27	12.62	3.85	0.87	0.76	5.69	0.52	0.40	0.09	0.14	100.75
Yavapai	Y.MC.523	0	3	0.86	63.78	16.60	8.68	2.54	2.35	2.80	1.95	0.71	0.23	0.08	100.58
Yavapai	Y.MC.524	0	3	2.19	59.79	19.36	8.56	1.91	1.52	0.76	3.98	0.75	0.21	0.09	99.12
Yavapai	Y.MC.525	0	3	2.50	57.94	19.35	7.95	2.50	2.54	2.09	3.48	0.95	0.22	0.09	99.61
Yavapai	Y.MC.526	0	3	0.75	65.33	14.65	7.65	2.57	3.36	2.76	1.81	0.58	0.28	0.08	99.82
<b>MEDIAN</b>				<b>1.54</b>	<b>63.78</b>	<b>16.60</b>	<b>7.95</b>	<b>2.50</b>	<b>2.35</b>	<b>2.76</b>	<b>1.95</b>	<b>0.71</b>	<b>0.22</b>	<b>0.09</b>	<b>99.82</b>
Texas Gulch	TG.PR.156.1	1	6	2.14	64.49	16.06	8.24	1.75	0.97	3.16	2.86	0.48	0.09	0.21	100.45
Texas Gulch	TG.PR.156.3	1	6	2.07	65.31	16.29	7.58	1.58	0.99	3.37	2.79	0.49	0.11	0.19	100.77
Texas Gulch	TG.PR.157	1	6	3.29	68.07	14.61	7.81	1.71	0.15	0.00	3.26	0.52	0.09	0.09	99.60
Texas Gulch	TG.M.164	1	7	2.81	62.09	18.43	8.15	1.64	1.04	1.49	3.03	0.78	0.15	0.12	99.73
Alder	COX.202	1	4	2.53	66.14	16.33	6.70	0.66	0.25	2.64	4.12	0.63	0.12	0.02	100.14
Alder	COX.203.2	1	4	3.45	60.76	18.96	8.16	2.14	0.28	1.15	3.43	0.67	0.16	0.21	99.37
Alder	COX.205	1	4	2.98	77.57	8.70	4.76	0.30	2.14	0.02	2.33	0.34	0.11	0.08	99.33
Alder	AL.TC.518	1	4	2.72	58.85	18.28	17.74	0.07	1.05	0.92	3.56	2.14	0.76	0.04	101.13
Alder	AL.TC.519	1	4	3.18	61.56	20.85	7.58	0.09	0.18	0.11	5.09	0.82	0.13	0.03	99.62
Alder	AL.TC.520	1	4	2.84	64.82	18.03	8.46	0.19	0.21	0.75	3.70	0.62	0.16	0.04	99.82
Alder	AL.TC.522	1	4	4.14	63.75	16.11	8.46	0.87	1.21	1.01	2.73	0.81	0.17	0.23	99.49
Alder	A.Y.651	1	5	3.80	63.50	19.26	7.01	1.13	0.27	0.44	4.37	0.75	0.21	0.05	100.78
Alder	A.Y.652	1	5	3.53	62.12	19.41	7.66	1.01	0.25	0.59	4.00	0.75	0.16	0.05	99.53
Alder	A.Y.654	1	5	3.44	61.72	19.33	7.87	1.12	0.23	0.40	4.32	0.83	0.20	0.07	99.53
Alder	A.Y.655	1	5	3.42	62.56	19.47	7.17	1.01	0.18	0.64	4.18	0.73	0.11	0.05	99.52
Alder	A.Y.658	1	5	3.62	60.96	21.19	7.43	0.95	0.22	0.95	4.22	0.66	0.15	0.05	100.40
Alder	A.Y.659	1	5	3.06	62.57	19.33	7.48	1.24	0.16	0.25	4.51	0.74	0.11	0.10	99.55
Alder	A.Y.660	1	5	3.28	61.00	19.62	8.20	1.42	0.22	0.32	4.39	0.76	0.16	0.10	99.47
Vallecito	V.DHC.278	1	13	2.23	59.95	18.78	11.78	0.54	1.37	0.99	2.69	0.86	0.25	0.02	99.46
Vallecito	V.DHC.280	1	13	2.62	62.73	16.48	8.71	0.90	1.86	0.00	4.80	0.58	0.74	0.06	99.48
Vadito	V.PF.431	1	9	1.16	67.50	13.75	8.17	1.06	1.82	1.87	3.40	1.15	0.16	0.10	100.14
Vadito	V.PF.432	1	9	2.07	63.08	15.24	10.60	1.13	1.70	0.61	3.58	1.39	0.25	0.09	99.74
Vadito	V.PF.434	1	9	1.40	65.33	14.55	9.27	1.13	4.09	1.13	1.71	1.21	0.23	0.21	100.26
<b>MEDIAN</b>				<b>2.98</b>	<b>62.73</b>	<b>18.28</b>	<b>8.15</b>	<b>1.06</b>	<b>0.28</b>	<b>0.75</b>	<b>3.58</b>	<b>0.75</b>	<b>0.16</b>	<b>0.08</b>	<b>99.62</b>
Uncompaghe	BC-4UF**	2		4.34	54.58	22.33	11.63	1.43	0.12	0.00	3.55	0.94	0.12	0.17	99.21
Uncompaghe	BC-5UF**	2		3.45	63.28	17.98	5.38	1.38	0.08	0.00	4.91	0.94	0.03	0.08	97.51
Uncompaghe	U.LC.288	2	19	9.06	73.33	11.37	0.57	0.77	0.03	0.00	2.91	0.50	0.05	0.01	98.60
Uncompaghe	U.LC.290	2	19	3.53	63.71	19.23	3.98	1.52	0.07	0.00	5.42	1.00	0.04	0.03	98.53
Uncompaghe	U.LC.291	2	19	2.10	76.27	14.46	1.38	0.35	0.03	0.00	3.60	0.66	0.01	0.01	98.87
Hondo	O.PS.127.1	2	11	4.81	81.20	7.80	1.03	0.49	0.42	0.00	2.13	0.37	0.21	0.02	98.48
Hess Canyon	WL.Y.J.181.2	2	17	3.57	63.25	17.64	8.48	0.96	0.15	0.00	4.78	0.84	0.02	0.02	99.71
Hess Canyon	WL.Y.J.182	2	17	3.59	48.04	24.77	15.35	0.21	0.07	0.00	6.98	1.08	0.05	0.00	100.14
Hess Canyon	WL.Y.J.185	2	17	4.90	50.47	17.84	19.17	2.26	1.27	0.00	2.20	0.71	0.93	0.45	100.20
Hess Canyon	BJ.BJ.190	2	17	2.44	67.52	15.83	5.19	1.28	0.61	1.61	4.41	0.60	0.12	0.05	99.66
Mazatzal	M.P.153	2	18	9.21	42.87	27.48	15.47	0.24	0.13	0.00	1.62	2.50	0.34	0.07	99.93
Mazatzal	M.TB.174	2	16	6.63	50.14	27.82	11.20	0.14	0.06	0.00	2.10	1.32	0.13	0.07	99.61
Mazatzal	MS.BC.194	2	14	3.50	69.30	14.55	7.20	1.55	0.09	0.00	2.49	0.63	0.03	0.08	99.42
Mazatzal	COX.210	2	14	2.99	66.11	17.99	4.22	1.03	0.46	1.63	3.65	0.70	0.06	0.09	98.93
Mazatzal	M.P.361	2	18	3.04	67.08	15.77	5.17	0.79	0.14	0.00	4.69	0.63	0.04	0.03	97.38
Mazatzal	MS.STC.436	2	15	3.20	68.43	16.44	4.18	1.39	0.15	0.57	3.67	0.71	0.04	0.05	98.83
Mazatzal	MS.STC.438	2	15	3.18	67.16	16.67	6.18	1.43	0.16	0.39	3.89	0.65	0.05	0.07	99.83
Mazatzal	MS.STC.440	2	15	3.62	64.29	19.60	3.88	1.22	0.15	0.25	4.93	0.73	0.04	0.04	98.75
Mazatzal	MS.STC.441	2	15	3.35	68.14	17.12	3.66	1.39	0.15	0.30	4.19	0.72	0.03	0.06	99.11
Mazatzal	DM.STC.442	2	15	3.91	64.31	21.85	8.01	0.00	0.04	0.00	0.45	0.89	0.04	0.01	99.51
Mazatzal	DM.STC.443	2	15	3.69	66.57	19.67	7.93	0.03	0.04	0.00	0.40	0.93	0.05	0.02	99.33
Mazatzal	MS.BC.448	2	14	5.68	41.87	28.02	12.24	3.10	0.11	0.00	6.79	1.29	0.04	0.09	99.23
Mazatzal	D.R.621	2	18	3.78	72.24	14.79	3.50	0.68	0.10	0.00	3.54	0.40	0.04	0.05	99.12
<b>MEDIAN</b>				<b>3.59</b>	<b>66.11</b>	<b>17.84</b>	<b>5.38</b>	<b>1.03</b>	<b>0.12</b>	<b>0.00</b>	<b>3.65</b>	<b>0.72</b>	<b>0.04</b>	<b>0.05</b>	<b>99.21</b>

We, therefore, define a ratio, the Index of Compositional Variability (ICV):

$$(\text{Fe}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O} + \text{CaO} + \text{MgO} + \text{MnO} + \text{TiO}_2)/\text{Al}_2\text{O}_3,$$

which measures the abundance of alumina relative to the other major cations in a rock or mineral. Silica is excluded to eliminate problems of quartz dilution. Nonclay silicates contain a lower proportion of  $\text{Al}_2\text{O}_3$  than clay minerals, relative to other constituents, therefore, they have a higher ICV. In addition, there is a compositional gradient within the nonclay silicates: the ICV tends to be highest in minerals high in the weathering sequence of Goldich (1938), such as the pyroxenes and amphiboles and decreases in more stable minerals such as the

alkali feldspars. The ICV decreases further in the montmorillonite group clay minerals and is lowest in the kaolinite group minerals (Fig. 5).

Because minerals show a relationship between resistance to weathering and ICV, the ICV may be applied to mudrocks as a measure of compositional maturity. **Compositionally immature mudrocks that contain a high proportion of nonclay silicate minerals, or that are rich in clay minerals such as montmorillonite and sericite will have high values of this index.** On the other hand, compositionally mature mudrocks, poor in nonclay silicates or dominated by minerals such as those of the kandite family, will have low values. Compositionally immature mudrocks tend to be found in tectonically active settings and are characteristi-

Table 2 continued.

Sequence	Sample	R	Loc. †	LOI	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub> *	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	Total
Apache Group	Ap.YR.470	3	25	4.12	45.29	28.16	12.98	0.71	0.07	0.36	7.96	1.14	0.05	0.01	99.45
Apache Group	Ap.RD.514	3	27	5.65	63.21	18.35	1.46	0.40	0.08	0.00	10.80	0.95	0.12	0.01	99.92
Grand Canyon	H.MC.535	3	22	1.55	68.67	13.69	5.59	0.71	0.25	0.00	8.49	0.63	0.13	0.02	94.83
Grand Canyon	H.MC.536	3	22	5.39	63.34	11.04	3.85	2.47	2.99	0.00	4.86	0.61	0.15	0.12	99.97
Grand Canyon	H.MC.536	3	22	5.39	63.34	11.04	3.85	2.47	2.99	0.00	4.86	0.61	0.15	0.13	94.83
Grand Canyon	S.C.545	3	22	2.76	68.06	15.70	5.64	0.83	0.15	0.00	5.48	0.65	0.60	0.02	99.97
Grand Canyon	H.TT.564b	3	22A	8.47	55.87	12.79	4.73	4.78	4.26	0.00	7.63	0.69	0.13	0.10	99.45
Grand Canyon	H.TT.565b	3	22A	7.32	58.36	12.87	4.97	4.14	3.37	0.00	8.02	0.65	0.13	0.09	99.92
Grand Canyon	H.TT.568b	3	22A	6.08	58.24	12.89	5.25	4.96	2.39	0.00	7.37	0.72	0.16	0.09	98.15
Grand Canyon	H.TT.562	3	22A	2.14	68.84	11.88	6.64	1.04	0.48	0.00	6.64	0.95	0.29	0.02	98.92
Grand Canyon	H.TT.563	3	22A	3.37	55.28	17.94	12.85	1.56	0.83	0.00	8.24	0.57	0.66	0.02	101.02
Grand Canyon	H.TT.564	3	22A	1.72	66.89	14.40	5.82	0.86	0.24	0.00	8.90	0.58	0.18	0.01	99.60
Grand Canyon	H.TT.577b	3	22A	2.09	60.52	17.44	7.71	0.99	0.23	0.00	9.51	0.75	0.15	0.01	99.40
Grand Canyon	H.PC.578b	3	23	7.74	55.59	13.03	5.98	4.00	3.87	0.00	8.48	0.71	0.18	0.10	99.64
Grand Canyon	H.PC.580b	3	23	12.46	50.04	11.09	5.56	5.91	7.16	0.00	6.73	0.63	0.12	0.15	96.85
Grand Canyon	H.PC.583	3	23	4.59	55.14	20.71	8.81	1.84	0.47	0.00	7.76	0.82	0.22	0.02	100.38
Grand Canyon	H.PC.585b	3	23	8.50	55.40	13.38	6.12	3.97	4.14	0.00	8.88	0.76	0.20	0.11	99.46
Grand Canyon	H.PC.586	3	23	2.95	65.82	13.83	7.44	1.37	0.47	0.00	6.70	0.73	0.22	0.03	99.36
MEDIAN					4.99	59.44	13.51	5.73	1.70	0.66	0.00	7.70	0.70	0.16	99.53
Ignacio	I.LC.254	4	40	3.72	62.55	19.07	3.26	1.48	0.15	0.00	8.02	1.04	0.03	0.02	99.34
Tapeats	T.J.365	4	28	5.62	48.58	24.71	10.11	1.01	0.18	0.00	7.15	1.96	0.25	0.03	99.60
Tapeats	T.GC.638	4	31	3.83	53.87	21.42	8.95	0.97	0.16	0.00	9.14	0.86	0.05	0.09	99.33
Tapeats	T.GC.639	4	31	5.62	54.42	21.50	9.36	1.16	0.07	0.00	6.47	1.16	0.10	0.02	99.88
Bright Angel	BA.PB.377	4	37	5.75	51.57	24.87	4.43	1.45	0.62	0.00	9.19	1.04	0.12	0.02	99.16
Bright Angel	BA.MC.531	4	38	6.05	50.83	27.25	3.79	1.19	0.16	0.00	8.44	1.01	0.18	0.02	98.92
Bright Angel	BA.MC.532	4	38	5.49	53.53	21.77	5.59	2.07	0.83	0.00	9.15	0.93	0.08	0.03	99.27
Bright Angel	BA.MC.533	4	38	5.44	56.41	22.40	5.16	0.76	0.55	0.00	6.99	1.05	0.42	0.08	99.26
Bright Angel	BA.PC.625	4	37	6.12	56.31	23.56	4.24	1.12	0.25	0.00	6.95	0.84	0.12	0.02	99.53
Bright Angel	BA.PC.626	4	37	5.85	55.34	22.29	5.99	2.02	0.20	0.00	6.88	1.04	0.07	0.04	99.72
Bright Angel	BA.PC.627	4	37	5.84	54.61	21.28	7.71	2.31	0.15	0.00	6.79	0.86	0.09	0.03	99.67
Bright Angel	BA.PC.628	4	37	6.14	53.78	22.29	7.35	2.36	0.22	0.00	7.05	0.88	0.10	0.03	100.20
Bright Angel	BA.PC.630	4	37	6.40	54.55	22.39	7.71	2.05	0.18	0.00	6.39	0.86	0.08	0.01	100.71
Bright Angel	BA.PC.631	4	37	6.04	52.47	21.53	9.33	2.50	0.15	0.00	7.23	0.92	0.12	0.04	100.33
Bright Angel	BA.PC.633	4	37	6.20	52.77	22.41	7.92	2.37	0.23	0.00	7.29	0.94	0.07	0.03	100.23
Bright Angel	BA.PC.634	4	37	6.01	54.94	20.39	6.79	2.72	0.70	0.00	7.22	1.03	0.07	0.06	99.93
Bright Angel	BA.PC.635	4	37	6.34	54.86	22.40	5.82	2.39	0.17	0.00	6.43	0.96	0.03	0.03	99.43
Bright Angel	BA.PC.637	4	37	7.63	48.15	31.33	2.56	0.87	0.16	0.00	6.79	1.38	0.12	0.02	99.01
MEDIAN					5.93	54.15	22.34	6.39	1.75	0.18	0.00	7.10	0.99	0.10	99.56
Dakota Set.	D.FC.217	5	42	8.14	79.72	11.58	0.38	0.07	0.17	0.00	0.36	0.89	0.01	0.01	99.13
Dakota Set.	D.FC.224	5	42	9.40	65.50	17.08	2.14	1.14	0.31	0.00	2.69	0.88	0.02	0.01	99.95
Dakota Set.	D.TC.225A	5	43	13.60	64.61	13.21	6.04	0.13	0.03	0.00	1.09	0.49	0.05	0.02	99.27
Dakota Set.	D.ARL.239	5	44	7.75	74.16	8.36	5.03	0.92	0.77	0.00	1.23	0.35	0.21	0.11	98.89
Dakota Set.	D.FC.250	5	42	10.42	61.90	19.18	2.80	1.11	0.13	0.00	2.85	0.72	0.12	0.01	99.04
Dakota Set.	D.BM.314	5	45	8.32	70.39	13.36	1.81	1.15	0.07	0.00	2.42	0.63	0.01	0.01	97.97
Dakota Set.	D.CB.337	5	46	9.92	61.99	21.02	2.06	0.83	0.18	0.00	2.42	0.74	0.03	0.01	99.20
Dakota Set.	D.CS.421	5	46	3.29	76.23	10.04	3.12	0.83	0.61	0.00	1.96	0.50	0.09	0.06	96.73
MEDIAN					8.86	67.95	13.29	2.37	0.88	0.18	0.00	2.19	0.65	0.04	99.00

†Locality numbers are keyed to Fig. 4, and to localities in Cox (1993)

\*Total iron is reported as Fe<sub>2</sub>O<sub>3</sub>(t)

\*\* Samples provided by D.A. Gonzales

cally first-cycle deposits (van de Kamp and Leake, 1985). Compositionally mature mudrocks characterise tectonically quiescent or cratonic environments (Weaver, 1989) where sediment recycling is active, but may also be produced by intense chemical weathering of first-cycle material (Barshad, 1966).

Another index of mudrock composition is the ratio  $K_2O/Al_2O_3$ . Clay minerals and feldspars have markedly different values for this ratio (Fig. 6), and so it can also be used as an indicator of the original composition of ancient mudrocks.

Trace element chemistry of mudrocks has been used in several studies to compare mudrocks of different ages or provenance or to establish the relative contribution of fractionated igneous material to the sedimentary system (e.g., Ronov and Migdisov, 1971; Taylor and McLennan, 1981, 1985; McLennan and Hemming, 1992). Many trace elements are ex-

tremely insoluble in aqueous systems, and tend, therefore, to be transferred from source rock to sediment without significant fractionation (Balashov et al., 1964; Nesbitt, 1979; Davies, 1980). Trace elements do not form mineral frameworks, but generally occur in association with clay minerals as sorbed particles on surfaces or included in interlayer cation sites; therefore, their occurrence in mudrocks is not strongly related to mineralogy and bulk composition. Further, most hydrothermal fluids have very low concentrations of insoluble trace elements such as the REE; hence, alteration of whole-rock trace element patterns during hydrothermal alteration and metamorphism is generally ineffective, except in cases where the ratio of water to rock is much greater than  $10^2$ – $10^3$  (Bau, 1991). Water-rock ratios on a regional scale during regional metamorphism are typically close to  $10^6$  (Ferry, 1983, 1988; Wood and Walther, 1986). For these reasons, ratios of low-

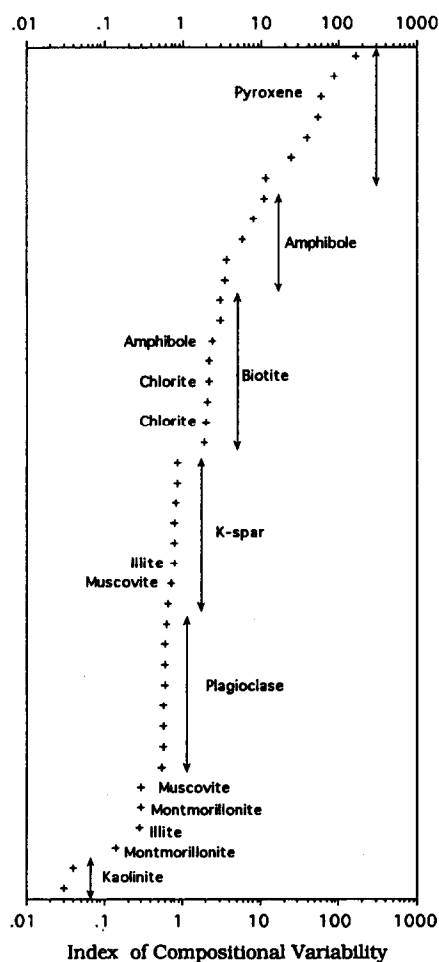


FIG. 5. Values for the Index of Compositional Variability (ICV)  $[(\text{Fe}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O} + \text{CaO} + \text{MgO} + \text{MnO} + \text{TiO}_2)/\text{Al}_2\text{O}_3]$  for selected rock-forming minerals. Crosses represent individual data values. Where a mineral name appears beside a data point, the value refers to that mineral. The arrows show the range of values for certain mineral groups; specific values from these groups are given by the crosses that are unaccompanied by a mineral name. Data from Deer et al. (1966). See text for explanation.

solubility trace elements in mudrocks generally reflect those of the source rocks (Cullers et al., 1975; Taylor and McLennan, 1985), making such trace elements a valuable tool for provenance analysis.

## 5. RESULTS AND DISCUSSION

### 5.1. Major Elements

The major element data are shown in Table 2 and Fig. 7. Statistically significant characteristics of the data fall into three categories: (1) progressive decrease or increase in abundance with time; (2) excursions from progressive trends; and (3) dog-leg patterns superimposed on an overall increase or decrease. In the following sections, these data will be presented, the mineralogical and provenance controls on the

trends discussed, and the trends analysed in terms of the tectonic evolution of the Colorado Province.

#### 5.1.1. Progressive secular trends

A first-order characteristic of the Colorado Province mudrocks is that several of the major oxides— $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ , and  $\text{MnO}$ —decline significantly in relative abundance through time (Fig. 7). The average ICV (Index of Compositional Variation) for Colorado Province mudrocks also declines (nonlinearly) as a function of time (Fig. 8). In contrast,  $\text{K}_2\text{O}$  shows a marked increase in relative abundance.

$\text{Al}_2\text{O}_3$  shows a statistically significant but poorly-defined increase in average abundance. An interesting feature of the  $\text{Al}_2\text{O}_3$  data distribution, however, is that in several respects it is the reverse of that of  $\text{SiO}_2$ . Although  $\text{SiO}_2$  shows no progressive trend, there are large, statistically significant fluctuations in its abundance through time. Samples from R0, R1, and R2 are statistically indistinguishable, but R3 and R4 samples are low in silica, and R5 mudrocks are on average richer in silica than any of the older samples (Fig. 7a). Fluctuations occur in the  $\text{Al}_2\text{O}_3$  data for R4 and R5 which are the reverse of those seen in the  $\text{SiO}_2$  data.

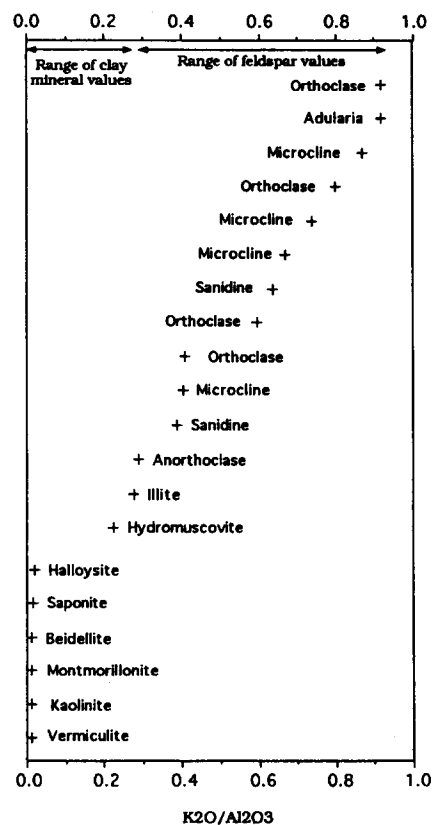


FIG. 6. Values of the  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$  ratio for K-feldspars and clay minerals. Crosses represent values for the specific minerals indicated. Data from Deer et al. (1966).



Because the dataset is closed (components sum to 100%), the close negative correlation between the alumina and silica data implies that large fluctuations in silica content may be masking more subtle trends in  $\text{Al}_2\text{O}_3$  abundance. To eliminate the effects of silica and to evaluate whether there are hidden trends in alumina content in these samples,  $\text{Al}_2\text{O}_3^*$  (= alumina as a percentage of the total analysis minus  $\text{SiO}_2$ ) was calculated. In contrast to the raw alumina data, there is a marked increase in the average abundance of  $\text{Al}_2\text{O}_3^*$  through time (Fig. 9).

### 5.1.2. Excursions from progressive trends

R3 mudrocks are commonly enriched in MgO, CaO, and  $\text{K}_2\text{O}$  relative to those from other sedimentation intervals (Fig. 7d,e,g). They have high values for the ICV and  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$  (Fig. 8). They are low in  $\text{SiO}_2$  (Fig. 7a), and in  $\text{Al}_2\text{O}_3^*$  (Fig. 9).

Values for  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$  (Fig. 8b) exceed those for illite, and lie in the range of values for alkali feldspars (Fig. 6). Values for the ICV (Fig. 8a) include the upper end of the range for feldspars (Fig. 5), but most samples have values well in excess of 1 (Fig. 8a). These data indicate that (1) the potassium content of these samples is controlled mainly by feldspar, and (2) in addition to feldspar, the original muds contained abundant mafic high-ICV minerals, either as detrital grains or in lithic fragments. Both detrital feldspar and volcanic lithic fragments are observed in thin sections of R3 mudrocks (Cox, 1993). The low values for  $\text{Al}_2\text{O}_3^*$  (Fig. 9) reflect the concomitant decrease in the proportion of clay minerals in R3 mudrocks.

R5 mudrocks have anomalously high  $\text{SiO}_2$  contents relative to the other sedimentation intervals (Fig. 7a), whereas the relative abundance of  $\text{Al}_2\text{O}_3$  is low (Fig. 7b). However, as has been discussed previously, the low  $\text{Al}_2\text{O}_3$  values are an artifact of the increase in silica; and  $\text{Al}_2\text{O}_3^*$  data demonstrate that, when the effect of silica is corrected for, R5 samples are not anomalous with respect to alumina content (Fig. 9). The high silica contents of R5 mudrocks are, therefore, attributed to quartz dilution. This is consistent with data from the laterally equivalent Mowry Shale in Wyoming, in which elevated silica contents have been shown to be due in part to the presence of abundant detrital quartz (Davis, 1970). Silt-sized detrital quartz is commonly observed in thin sections of R5 mudrocks (Cox, 1993).

The low  $\text{K}_2\text{O}$  content of these samples (Fig. 7g) is ascribed to intense chemical weathering. During the Cretaceous in the southwestern United States the climate was subtropical and humid, and weathering was intense (Bejnar and Lessard, 1976; Kauffman, 1977). These conditions, which promote leaching of soils and removal of alkalis in solution, provide the best explanation for the radical decrease in  $\text{K}_2\text{O}$  abundance and low overall concentration of oxides other than  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in R5 mudrocks. Kaolinite is very common in Cretaceous mudrocks, and its abundance has been interpreted to reflect efficient chemical weathering (Finkelstein et al., 1990; Leckie et al., 1991).

### 5.1.3. Dog-leg overprints on progressive trends

For some oxides, statistically significant progressive trends may be resolved into two distinct subrends. MgO, CaO, and ICV values decline, are rejuvenated in R3, and then decrease again (Figs. 5, 6a).  $\text{Al}_2\text{O}_3^*$  values increase from R0 to R2, decrease in R3, then rise again from R3–R5 (Fig. 9). These distributions are interpreted to mean that there is episodic input of first-cycle material with high ICV values, followed by periods dominated by recycling and reworking of this material to produce mudrocks with progressively more mature compositions. The basis for this interpretation will be discussed below.

The  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$  ratio reaches a maximum in R3 and declines thereafter, and is interpreted to reflect an initial phase in which little K-feldspar was available, followed by massive input of granitic material in R3, with subsequent recycling-dominated sedimentation.

## 5.2. Interpretation of Major Element Trends in Colorado Province Mudrocks

The overall picture that emerges from the data is that older Colorado Province mudrocks tend to have highly variable compositions and younger ones to have more restricted compositions, dominated by potash and alumina (Fig. 7). Superimposed on this are compositional anomalies, or second-order excursions from the general trend, as discussed above.

There is a progressive decrease in average LOI values in older samples (Table 2), which is the expected consequence of loss of volatiles through compaction and dewatering. This is the only compositional trend in these rocks which may be attributed to diagenesis: in all other cases where a compositional trend is present, it is the opposite of that which would be predicted to result from diagenetic alteration. Generally, the oldest samples have the highest concentrations of the most mobile elements. The trends visible in the data must, therefore, be the result of real differences in original composition between mudrocks of different ages.

### 5.2.1. Causes of major element variation

The major element composition of mudrocks reflects their primary mineralogy, which is sensitive to the intensity of chemical weathering. Progressive weathering during erosion and transport tends to increase the abundance of cation-poor clays and oxides of iron and aluminium at the expense of both nonclay detrital minerals and compositionally complex clays (Barshad, 1966; Tardy et al., 1973; Heckrodt and Bühlmann, 1987; Middleburg et al., 1988; Weaver, 1989). The smectites, chlorites, and other mixed-layer clays which house Ca, Na, Fe, and Mn degrade quickly during weathering, breaking down into compositionally more simple clays such as the kaolinites. Elements released during this process tend to be leached, and the ultimate product is a mud depleted in soluble components and enriched in Al and Fe (Makolm et al., 1969; Hayes, 1970; McKeague and Brydon, 1970; Herbillon and Makumbi, 1975; Potter et al., 1975; Fanning and Keramidas, 1977; Weaver, 1989).

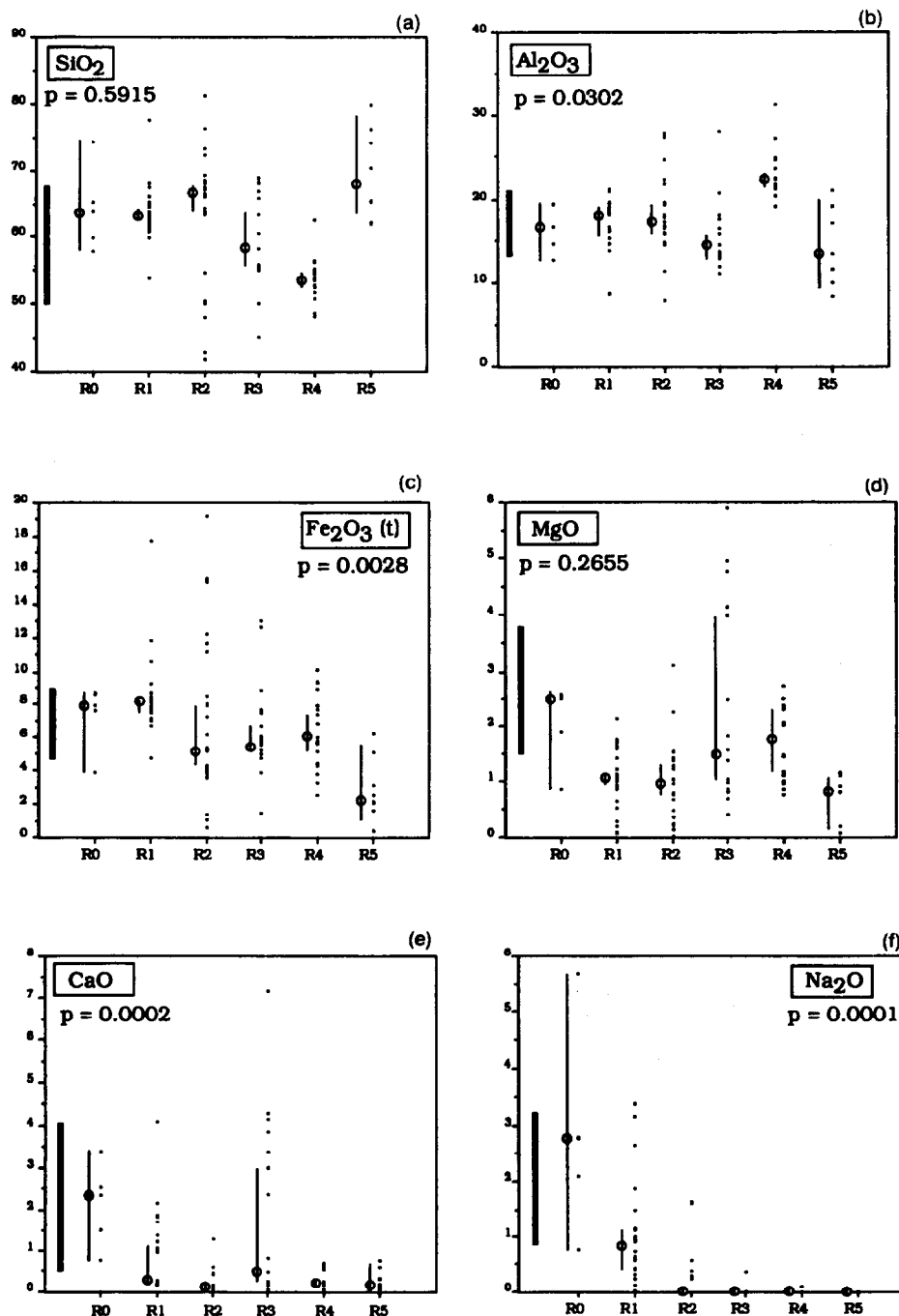


FIG. 7. Abundance of major elements as a function of sedimentation interval. Data are recalculated volatile-free. Dots represent individual data points. Circles represent group medians. Vertical bars represent errors on the estimated averages at a confidence level of  $\approx 95\%$  (see text). The p statistic shown on each graph measures the probability that the slope of a regression line through the data is zero. The smaller the number, the higher the probability that the line slope is non-zero: i.e., data distributions with p values of 0.0500 or less show time-related trends that are significant at or above the 95% level. Data distributions with values greater than 0.0500 do not show significant trends. The approximate range of compositions for continental island arc mudrocks, based on data from Bhatia (1985) and van de Kamp and Leake (1985) is shown by the thick black line on the left side of each graph.

Although K has a high aqueous solubility, it tends to be conserved in mudrocks because of the chemical stability of illite. Illites are resistant to weathering and are quite stable in soils except under extreme weathering conditions (Norris

and Pickering, 1983). Therefore, muds derived by recycling of older sediments generally contain a high proportion of illite (Potter et al., 1975; Potter et al., 1980), and are consequently very potassic.

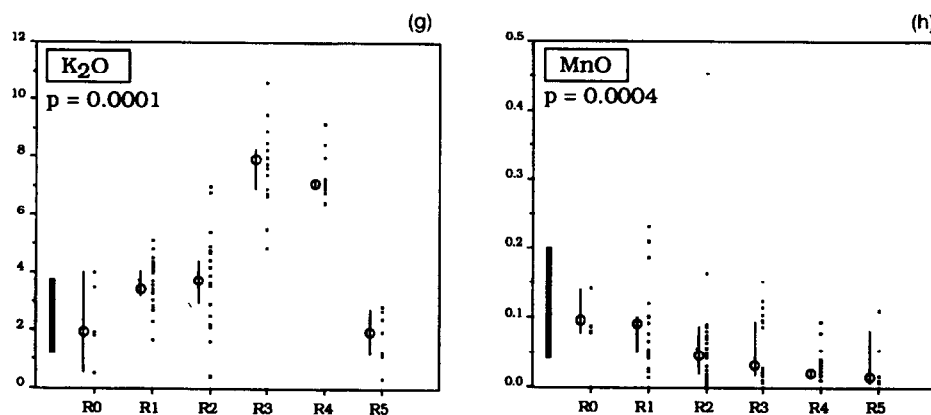


FIG. 7. (Continued)

The abundance of MgO, MnO, CaO, Na<sub>2</sub>O, and Fe<sub>2</sub>O<sub>3</sub>(t) in rocks of the basement (R0) and early cover (R1) is consistent with the immature character of these sediments, which were largely derived from arc-related volcanic and plutonic rocks (Anderson, 1989a; Bauer and Williams, 1989). The average ICV values for R0 (1.1) and R1 (1.0) (Fig. 8a) exceed the range of values for the common clay minerals (0.03–0.78) and feldspars (0.54–0.87) (Fig. 5), indicating that these samples contained abundant non-clay silicate minerals with high ICV values.

The subsequent decline in the relative abundance of CaO, Na<sub>2</sub>O, MgO, and Fe<sub>2</sub>O<sub>3</sub> probably reflects the decrease in both nonclay silicate minerals and compositionally immature clay minerals (such as the montmorillonite group minerals) in Colorado Province mudrocks. Mudrocks from subsequent sedimentation intervals (with the exception again of R3) have on average lower values (Fig. 8), approaching or within the range of clay mineral ICV values, indicating that later mudrocks contained lower proportions of nonclay silicates, and were dominated by clay minerals. The increase through time in the relative proportion of K<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub>\* is likewise interpreted to reflect an increase in the proportion of compositionally mature, alumina-rich clay minerals.

The overall trend away from compositions rich in Ca, Na, Fe, and Mn, towards more compositionally mature, potassic mudrocks is, therefore, consistent with the emergence of a recycling-dominated sedimentary system during the tectonic evolution of the Colorado Province.

These patterns are unlikely to simply reflect erosion of progressively more felsic basement. In the first place, the values for K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> for several intervals, most notably R4 and R5, are well below those for feldspar, indicating that little or no detrital K-feldspar was present in these sediments. Secondly, TiO<sub>2</sub> abundance is much lower in felsic than in mafic rocks, so that mudrocks derived from progressively more felsic source rocks would be expected to have decreasing amounts of TiO<sub>2</sub>. In contrast, TiO<sub>2</sub> in Colorado Province mudrocks remains approximately constant through time (Table 2). Titanium is a very insoluble element, which tends to be conserved in mudrocks, and its distribution in these samples im-

plies that recycling of older Ti-rich detritus is an active process in the Colorado Province.

The pattern of increasing overall maturity is complicated by excursions from the compositional trends, mainly at R3, and by the dog-leg patterns for some oxides. These may be explained by episodic rejuvenation of the sedimentary system by basement uplift, which provides an influx of first-cycle material. This interpretation is supported by a consideration of the differences between the composition of the R3 and R0/R1 mudrocks.

Both the oldest Colorado Province mudrocks (R0 and R1) and those from R3 are characterised by a significant proportion of (presumably) first-cycle silicate detritus, indicated by the high ICV values and the abundance of Ca, Fe, Mg, etc. Examination of the ICV and the K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio, however, indicate that there are distinct differences in the composition of the nonclay silicate fraction in the R0/R1 and R3 mudrocks; the older mudrocks have a high average ICV, but low values for K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub>, in contrast to the high ICV and high K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> of the R3 samples. This indicates that the nonclay silicate material in the R3 rocks was dominated by K-feldspar, whereas the R0 and R1 samples contained little K-feldspar but an abundance of sodic, calcic, and ferric silicate minerals.

Mudrocks of R0 and R1 were derived from orogenic arc-related source rocks, including a high proportion of mafic volcanic rocks, at an active plate margin (Gastil, 1958; Reed, 1988; Mawer et al., 1990). R3 rocks, on the other hand, were formed on stable continental crust, and received detritus from mid-Proterozoic post orogenic granites, which were exposed throughout the Colorado Province by Late Precambrian uplift (Elston, 1989; Wrucke, 1989). In the R0 and R1 rocks the primary constituents have not survived metamorphism and are represented now by biotite, chlorite, and iron oxide; but in R3 preservation is better and K-feldspar can be detected both by XRD analysis and in thin section (Cox, 1993).

The difference between the first-cycle component in R0/R1 and R3 is nicely demonstrated by Fig. 10, which shows the averages for each sedimentation interval on a molar proportions plot of Al<sub>2</sub>O<sub>3</sub>-CaO + Na<sub>2</sub>O-K<sub>2</sub>O (Nesbitt and Young, 1984). The data points define a dog-legged track from a start-

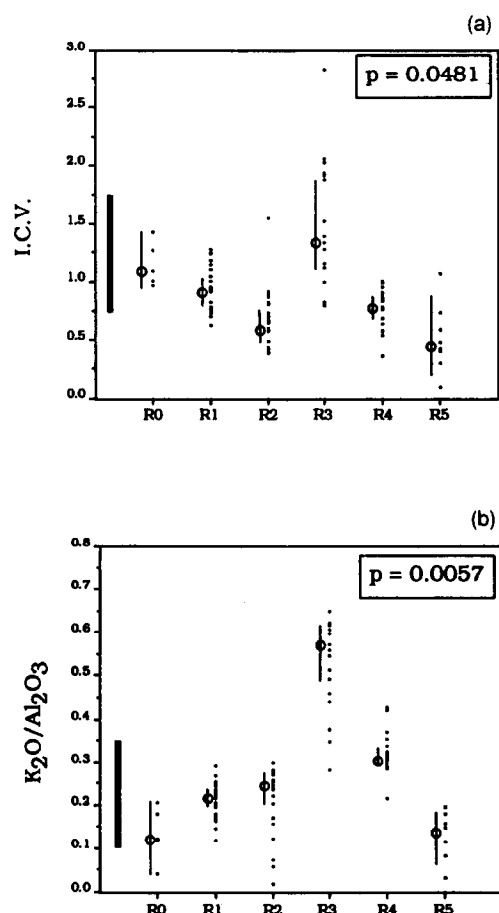


FIG. 8. Major element ratios (volatile free) as a function of sedimentation interval. Small dots are individual data points. Circles represent group medians, and error bars represent  $\approx 95\%$  confidence intervals about the averages. For explanation of p statistic, see caption to Fig. 7. The thick black line on the left side of each graph shows the approximate range of compositions for island arc mudrocks (data from Bhatia, 1985, and van de Kamp and Leake, 1985). (a) The Index of Compositional Variability (ICV):  $(\text{Fe}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O} + \text{CaO} + \text{MgO} + \text{MnO} + \text{TiO}_2)/\text{Al}_2\text{O}_3$ . (b) Ratio of  $\text{K}_2\text{O}$  to  $\text{Al}_2\text{O}_3$ .

ing point close to the composition of tonalite, towards the muscovite-kaolinite join, with an excursion at R3 to compositions close to granite. In effect this track is tracing the tectonic development of the Colorado Province sedimentary system from an arc-dominated period, through a period of reworking to a major basement uplift event, followed by a long interval of recycling-dominated sedimentation.

### 5.3. Trace Elements

Complete trace element analyses are presented in Table 3. Younger Colorado Province mudrocks tend to be enriched in the incompatible high field-strength elements (HFSE) and depleted in compatible transition elements relative to older samples. This tendency is illustrated by the ratios in Fig. 11. There is no correlation between the aqueous solubilities of the ele-

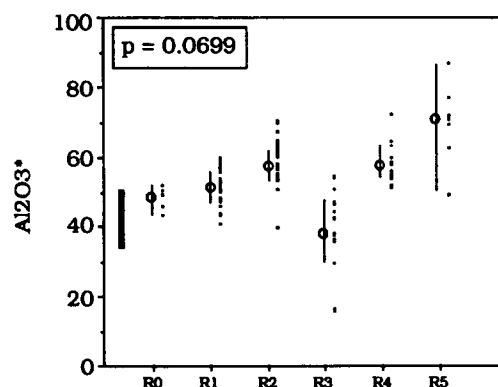


FIG. 9. Abundance of  $\text{Al}_2\text{O}_3^*$  (see text for derivation), plotted as function of sedimentation interval. Dots are individual data points. Circles represent group medians, and error bars represent 95% confidence intervals on the averages. For explanation of p statistic, see caption to Fig. 7. The thick black line on the left of the graph shows the approximate range of compositions for island arc mudrocks (data from Bhatia (1985) and van de Kamp and Leake (1985)).

ments concerned (Riley and Skirrow, 1975; Broecker and Peng, 1982) and the trends in the data. Although some highly soluble elements (e.g., Sr, Ba) are depleted, other elements that are mobile in weathering systems (most noticeably Li) increase in abundance through time (Table 3). It is, therefore, difficult to invoke progressive weathering or any recycling

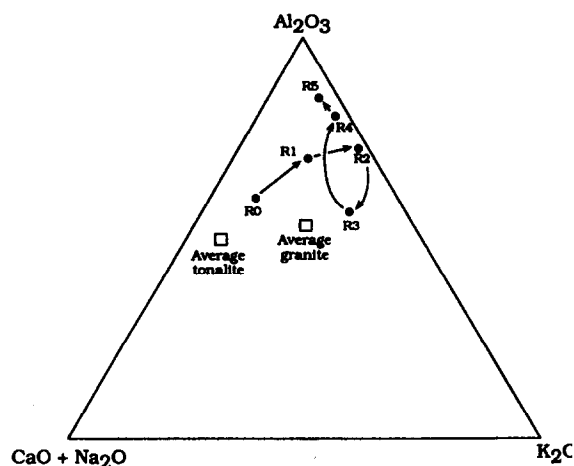


FIG. 10. Average for each sedimentation interval shown on a proportions plot of  $\text{Al}_2\text{O}_3\text{-CaO}^* + \text{Na}_2\text{O-K}_2\text{O}$  (Nesbitt and Young, 1984).  $\text{CaO}^*$  is defined as CaO in silicates only. However, there is no objective way to distinguish carbonate CaO from silicate CaO, so total CaO is plotted here. This is justified on the basis that none of the samples appeared calcareous, and all samples contained less than 5 wt% CaO. The effect of inclusion of non-silicate carbonate would be to enhance the apparent immaturity of a sample by pushing the data point towards the  $\text{CaO} + \text{Na}_2\text{O}$  corner. Values for average tonalite and average granite are from Nesbitt and Young (1984).

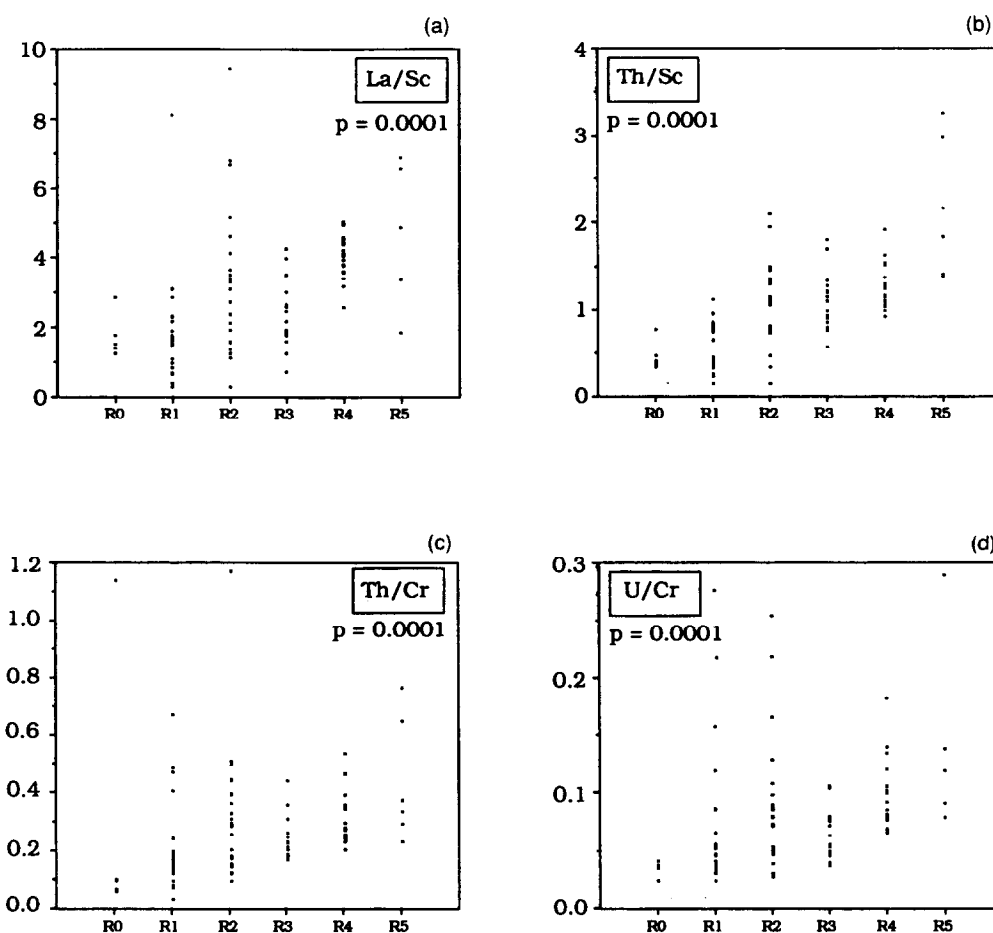


FIG. 11. Selected trace element ratios for Colorado Province mudrocks. For explanation of p statistic, see caption to Fig. 7. Complete analyses are presented in Table 3.

related process. Another possible control, increases in the amount of organic material in the sedimentary system through time, is also unlikely, because those elements analysed which have an affinity for organic material have dissimilar distributions: U increases through time, V decreases, and Ni shows no significant trend (Table 3).

The distribution of the trace elements seems on the whole to be related to their igneous chemistry rather than their aqueous or organic chemistry, which implies that the data reflect the input of first-cycle material, and that the increasing abundance of HFSE relative to transition metals records an increase in granitic source rocks through time.

Several of the incompatible elements (Rb, Th, Hf, Zr, U) show significant progressive increase in abundance over time. In contrast, the compatible elements tend to have more irregular distributions, and do not show progressive increases or decreases through time (Table 3). Incompatible elements increase because they are being actively added to the sediment mass through time as the first-cycle input becomes dominated by granitic material (Fig. 3). Input of compatible trace elements to the sedimentary system, however, becomes negli-

gible over time; but because of the low solubilities of the metals involved, little is fractionated into the dissolved load of the transporting medium as older mudrocks are recycled. Low solubility transition metals such as Cr and Sc, which were introduced to the sedimentary system mainly in R0 or R1 time, will tend to be retained by clay particles during recycling (Ermolenko, 1972; Roaldset, 1973, 1978; Davies, 1980; Fleet, 1984; Salomons and Forstner, 1984; Horowitz and Elrick, 1987; Middleburg et al., 1988; Horowitz, 1991; Keizer and Bruggenwert, 1991). Therefore, in spite of the decline in input of these metals, their time-related decrease in concentration is not significant.

#### 5.4. Rare Earth Elements

Rare earth element analyses are presented in Table 4. Eu/Eu\*, which measures the size of the europium anomaly (see caption to Fig. 12 for derivation), shows a marked decrease over time, and  $\Sigma\text{REE}_n$ ,<sup>†</sup> which is the sum of REE in a sample

<sup>†</sup> Subscript n denotes data normalised to chondrites.

Table 3. Trace element concentrations in ppm for mudrocks from the Colorado Province.

Sequence	Sample	R	Loc.*	Rb	Ba	Th	HI	Sc	Cr	Zr	Y	Sr	U	Pb	Zn	Cu	Ni	V
Ash Creek	AC.J.139.1	0	1	4	143	7.8	5.0	10	7	223	33	115	4.3	6	99	19	3	14
Yavapai	Y.MC.523	0	3	89	298	5.5	3.6	17	88	154	17	273	3.0	17	85	33	33	126
Yavapai	Y.MC.524	0	3	127	802	7.3	3.3	21	75	143	19	309	3.0	18	108	42	42	120
Yavapai	Y.MC.525	0	3	80	1380	8.3	4.3	22	142	190	20	588	3.3	17	115	84	40	143
Yavapai	Y.MC.526	0	3	79	394	6.2	2.3	14	86	108	13	546	2.4	18	56	86	30	107
<b>MEDIAN</b>				<b>80</b>	<b>394</b>	<b>7.3</b>	<b>3.6</b>	<b>17</b>	<b>75</b>	<b>154</b>	<b>19</b>	<b>309</b>	<b>3.0</b>	<b>17</b>	<b>99</b>	<b>42</b>	<b>33</b>	<b>120</b>
Texas Gulch	TG.PR.156.1	1	6	72	628	4.9	1.4	23	38	93	13	160	2.0	19	62	57	11	124
Texas Gulch	TG.PR.156.3	1	6	66	679	4.8	2.1	22	37	95	12	163	3.1	17	58	34	13	123
Texas Gulch	TG.PR.157	1	6	69	177	3.7	2.0	17	50	123	17	38	2.3	21	285	56	42	142
Texas Gulch	TG.PR.157	1	6	24	413	0.8	3.3	2	28	16	19	71	1.8	26	37	27	2	38
Texas Gulch	TG.M.164	1	7	145	641	7.5	3.3	21	81	159	17	309	1.9	23	109	4	45	125
Alder	COX.202	1	4	170	340	14.3	3.9	13	60	180	22	27	1.7	15	88	5	36	51
Alder	COX.203.2	1	4	161	717	11.7	4.0	19	76	178	25	178	2.8	20	108	92	47	89
Alder	COX.205	1	4	109	326	6.8	2.5	9	35	101	12	79	2.9	10	58	10	41	86
Vallecito	V.DHC.278	1	13	65	546	5.8	3.5	24	86	152	24	347	2.6	14	34	32	47	239
Vallecito	V.DHC.280	1	13	98	1502	4.6	2.8	15	59	118	23	236	1.9	25	32	13	14	208
Vadito	V.PF.431	1	9	128	825	11.1	9.0	18	24	316	60	91	2.8	16	137	17	24	100
Vadito	V.PF.432	1	9	112	1390	7.2	8.3	21	18	322	57	105	2.8	12	147	62	18	131
Vadito	V.PF.434	1	9	73	701	8.0	8.0	20	12	317	56	188	2.7	16				
Alder	AL.TC.518	1	4	163	1158	5.7	5.5	42	12	233	70	197	3.3	27	55	34	18	382
Alder	AL.TC.519	1	4	241	790	13.9	5.0	19	122	210	30	151	4.2	24	56	17	33	118
Alder	AL.TC.520	1	4	226	581	13.4	4.0	17	99	151	28	164	3.5	22	52	44	34	106
Alder	AL.TC.522	1	4	151	624	9.2	3.9	22	122	166	31	136	3.9	18	103	16	80	86
Alder	A.Y.651	1	5	211	588	12.9	4.5	17	88	183	28	127	2.5	19	61	5	35	111
Alder	A.Y.652	1	5	216	529	13.3	4.7	16	82	202	32	137	4.4	20	64	19	47	110
Alder	A.Y.654	1	5	199	591	15.3	5.4	16	84	228	31	113	4.3	18	73	9	40	106
Alder	A.Y.655	1	5	196	563	13.3	4.5	17	89	190	29	137	3.5	23	63	11	39	109
Alder	A.Y.658	1	5	296	651	13.3	4.0	18	77	166	34	129	3.5	23	73	16	38	98
Alder	A.Y.659	1	5	235	569	13.3	5.0	18	90	196	29	137	4.7	19	87	8	44	104
Alder	A.Y.660	1	5	252	565	15.6	5.2	19	94	205	36	143	4.2	20	101	11	46	105
<b>MEDIAN</b>				<b>155</b>	<b>608</b>	<b>9.7</b>	<b>4.0</b>	<b>18</b>	<b>77</b>	<b>179</b>	<b>29</b>	<b>138</b>	<b>2.9</b>	<b>20</b>	<b>64</b>	<b>17</b>	<b>38</b>	<b>108</b>
Uncompaghe	BC-4UF**	2								179	45	55	7.3	21	139	12	43	181
Uncompaghe	BC-5UF**	2		214	637	15.7	8.8	20	89	331	35	45	14.8	40	120	14	24	107
Hondo	O.PS.127.1	2	11	93	778	5.0	3.1	15	56	122	10	85	3.9	12	10	104	5	139
Hondo	O.PS.127.2	2	11	90	663	5.1	3.7	11	45	159	7	182	3.9	13	12	44	5	184
Mazatzal	M.P.153	2	18	38	372	61.0	31.0	42	162	1098	178	1093	15.7	55	72	61	39	134
Mazatzal	M.TB.174	2	16	69	334	33.4	10.9	16	68	433	78	491	6.0	45	36	20	19	36
Hees Canyon	WLY.J.181.2	2	17	219	619	21.0	8.4	19	18	332	32	47	3.9	14	62	8	37	114
Hees Canyon	WLY.J.182	2	17	366	846	21.4	7.5	28	150	290	47	164	6.9	29	19	9	19	161
Hees Canyon	WLY.J.185	2	17	130	289	14.1	4.4	20	84	151	63	35	2.4	18	179	142	38	92
Hees Canyon	BJ.BJ.190	2	17	207	968	17.4	6.0	12	45	238	36	86	3.2	15	84	9	25	61
Mazatzal	MS.BC.193	2	14	147	628	14.0	5.6	11	36	232	32	58	3.0	12	66	17	14	61
Mazatzal	MS.BC.194	2	14	107	417	14.1	6.3	11	49	270	36	47	2.4	9	131	18	21	57
Mazatzal	COX.210	2	14	166	902	20.0	7.1	14	46	300	50	157	3.8	12	69	22	21	63
Uncompaghe	U.LC.288	2	19	89	457	8.7	4.5	12	62	210	51	123	15.7	19	9	12	26	278
Uncompaghe	U.LC.290	2	19	217	689	16.5	10.0	24	136	370	46	47	5.0	7	61	24	33	109
Uncompaghe	U.LC.291	2	19							413	29	70	4.8	6	19	9	11	83
Mazatzal	M.P.361	2	18	360	795	17.5	7.0	12	49	274	32	81	4.2	20	84	11	22	49
Mazatzal	MS.STC.436	2	15	181	672	17.1	7.0	13	53	267	35	78	4.1	8	66	65	23	70
Mazatzal	MS.STC.438	2	15	185	557	16.8	6.8	13	55	253	40	59	4.3	15	74	33	19	63
Mazatzal	MS.STC.440	2	15	191	556	19.8	6.9	15	71	268	45	59	3.3	14	67	66	29	86
Mazatzal	MS.STC.441	2	15	168	555	15.6	7.3	14	62	286	41	58	2.3	22	67	36	23	79
Mazatzal	DM.STC.442	2	15	22	168	18.5	5.6	153	124	220	56	96	3.3	15	18	13	9	46
Mazatzal	DM.STC.443	2	15	21	132	17.8	7.4	17	50	298	64	146	5.3	15	25	18	25	46
Mazatzal	MS.DC.448	2	14	302	771	25.1	14.0	22	126	571	66	40	6.6	17	132	36	43	130
Mazatzal	D.R.621	2	18	240	519	11.9	5.3	12	27	208	28	57	3.4	17	99	14	23	36
<b>MEDIAN</b>				<b>168</b>	<b>618</b>	<b>17.1</b>	<b>7.0</b>	<b>15</b>	<b>56</b>	<b>270</b>	<b>41</b>	<b>70</b>	<b>4.1</b>	<b>15</b>	<b>66</b>	<b>18</b>	<b>23</b>	<b>83</b>

relative to the sum in chondrites, increases in younger samples.

The rare earth element patterns support the hypothesis that trace element compositions track changes in the composition of crystalline input to the sedimentary system (Fig. 12). Europium is not fractionated during weathering or diagenesis relative to the other REE (see McLennan, 1989, for review); therefore, the increasing size of the europium anomaly in younger mudrocks must reflect input from source rocks with increasingly large Eu anomalies or from an evolving mixture of rocks with differing Eu anomalies. The REE are strongly incompatible elements which are concentrated in partial melts, and so should be enriched in sediments derived from granitic rocks. The increases in total REE content relative to chondrites, therefore, reflect the increasing importance of

fractionated igneous material in the source rocks for Colorado Province mudrocks.

### 5.5. Differences between Major and Trace Element Behaviour in Mudrocks

The conclusion that trace element distributions are controlled by the composition of first-cycle input is at odds with the major element data, which are sensitive to the relative proportion of first-cycle and recycled material in addition to discriminating between mafic and felsic crystalline input. This decoupling of the behaviour of the major elements and the insoluble trace elements may be explained by their differing susceptibilities to fractionation during weathering and transport. Previous studies have shown that the major element

Table 3 Continued

Sequence	Sample	R	Loc.*	Rb	Ba	Th	Hf	Sc	Cr	Zr	Y	Sr	U	Pb	Zn	Cu	Ni	V
Apache	Ap.YR.470	3	25	320	1360	26.3	6.7	20	155	253	37	230	6.0	49	37	19	21	140
Apache	Ap.RD.514	3	27	159	310	10.4	6.9	19	59	279	45	26	2.7	15	7	33	14	88
Grand Canyon S.	H.MC.535	3	22	174	574	10.6	4.7	13	52	185	27	36	1.9	9	24	18	26	74
Grand Canyon S.	H.MC.536	3	22	125	393	7.7	6.5	7	37	262	27	40	1.8	12	21	17	25	57
Grand Canyon S.	S.C.545	3	22A	233	259	17.8	8.5	11	41	304	25	154	4.2	12	37	9	25	29
Grand Canyon S.	H.TT.554b	3	22A	151	445	8.9	4.8	11	40	199	36	65	3.6	11	45	24	24	59
Grand Canyon S.	H.TT.555b	3	22A	147	394	12.6	6.1	10	36	244	42	53	2.7	13	41	19	25	56
Grand Canyon S.	H.TT.558b	3	22A	149	389	10.3	6.5	11	46	263	44	66	3.6	15	64	20	32	68
Grand Canyon S.	H.TT.562	3	22A	191	345	13.7	8.4	8	69	332	36	44	3.2	15	26	25	19	85
Grand Canyon S.	H.TT.563	3	22A	321	419	14.6	4.3	16	83	167	35	70	5.1	18	40	13	38	189
Grand Canyon S.	H.TT.564	3	22A	155	442	12.1	3.8	11	50	154	210	31	2.7	8	23	19	44	107
Grand Canyon S.	H.TT.577b	3	22A	170	469	10.9	3.9	14	54	186	37	66	2.8	8	13	10	35	110
Grand Canyon S.	H.PC.578b	3	23	169	327	10.0	5.3	11	44	213	35	44	3.1	15	42	17	27	70
Grand Canyon S.	H.PC.580b	3	23	108	226	6.3	3.5	9	34	172	29	65	2.5	15	38	15	26	61
Grand Canyon S.	H.PC.583b	3	23	248	461	17.4	5.2	23	106	203	42	61	4.7	10	42	13	44	127
Grand Canyon S.	H.PC.585b	3	23	244	392	14.0	5.6	12	46	224	31	129	3.5	16	41	19	29	70
Grand Canyon S.	H.PC.586	3	23	227	346	14.8	6.3	13	58	266	35	55	3.1	13	37	24	24	67
MEDIAN				170	393	12.1	5.6	11	50	224	36	61	3.1	13	37	19	26	70
Ignacio	I.LC.254	4	40	221	839	16.2	10.5	15	71	478	42	163	5.3	20	76	11	30	81
Tapeats	T.J.365	4	28	332	557	38.0	20.0	24	83	785	86	1061	10.9	29	88	24	40	119
Bright Angel	BA.PB.377	4	37	307	447	26.6	7.2	21	97	314	51	398	7.6	26	51	36	26	113
Bright Angel	BA.MC.531	4	38	255	414	20.0	6.6	22	84	282	43	511	8.4	24	65	20	30	123
Bright Angel	BA.MC.532	4	38	315	470	20.2	4.7	17	84	197	36	176	5.7	19	81	9	40	108
Bright Angel	BA.MC.533	4	38	174	376	20.1	6.7	16	58	326	60	498	8.0	27	57	50	28	114
Bright Angel	BA.PC.625	4	37	253	490	22.9	6.8	17	79	263	46	287	6.0	21	64	25	30	92
Bright Angel	BA.PC.626	4	37	237	477	22.2	5.8	18	83	237	51	211	6.6	19	105	17	43	104
Bright Angel	BA.PC.627	4	37	267	508	21.1	7.5	19	80	180	41	188	6.0	18	107	32	39	104
Bright Angel	BA.PC.628	4	37	261	449	19.6	4.4	19	83	233	40	186	5.4	18	106	42	42	94
Bright Angel	BA.PC.630	4	37	262	580	21.2	6.2	21	85	260	58	156	6.6	34	105	33	45	91
Bright Angel	BA.PC.631	4	37	271	484	18.2	5.1	19	91	234	47	189	5.8	41	110	154	38	109
Bright Angel	BA.PC.633	4	37	459	28.6	14.2	19	74	729	101	161	7.7	33	109	10	46	101	
Bright Angel	BA.PC.634	4	37	265	601	24.7	8.5	17	73	361	49	130	6.1	25	99	9	40	97
Bright Angel	BA.TT.635	4	37	219	536	22.0	5.6	20	80	256	45	229	7.8	25	101	24	44	102
Bright Angel	BA.PC.637	4	37	243	594	32.2	12.4	26	91	596	104	627	16.4	38	70	26	45	187
Tapeats	T.GC.638	4	31	373	946	30.2	21.7	16	57	709	55	390	6.7	26	55	10	32	112
Tapeats	T.GC.639	4	31	262	487	24.6	9.4	22	73	367	66	482	6.6	23	63	13	40	121
MEDIAN				262	489	22.1	7.0	19	81	298	50	220	6.6	25	85	24	40	106
Dakota	D.FC.217	5	48	15	131	19.8	17.0	6	26	683	40	26	7.5	21	25	11	9	28
Dakota	D.FC.224	5	42	144	337	16.6	5.8	12	74	224	31	64	10.1	8	97	29	20	102
Dakota	D.TC.225A	5	42							138	17	103	2.6	19	14	21	15	65
Dakota	D.AR.239	5	43	63	181	11.4	6.7	6	35	234	25	454	4.1	14	112	15	17	37
Dakota	D.FC.250	5	44							205	26	69	7.4	12	91	36	23	141
Dakota	D.BM.314	5	42							268	23	59	4.7	9	61	19	18	90
Dakota	M.PRL.329	5	45	140	255	17.7	5.0	13	62	193	23	62	4.8	8	96	23	24	113
Dakota	D.CB.337	5	46							267	28	84	4.3	16	46	16	11	82
Dakota	D.CS.420	5	46	75	151	28.9	10.6	10	45									
Dakota	D.CS.421	5	46	76	822	13.2	10.7	6	36	400	28	66	3.2	17	58	33	18	42
MEDIAN				76	218	17.2	8.7	8	41	234	26	66	4.7	14	61	21	18	82
p value				.0046	.0021	.0001	.0004	.2807	.6650	.0014	.0863	.6435	.0003	.6670	.1703	.2530	.3046	.0700
Trends (>95% significance)				inc.	dec.	inc.	inc.	none	none	inc.	none	none	inc.	none	none	none	none	dec.

\*Locality numbers keyed to Fig. 4 and to localities in Cox (1993)

\*\*Samples provided by D.A. Gonzales

composition and mineralogy of fine-grained sediments are governed more strongly by the extent of weathering than by source rock composition (Barshad, 1966; Tardy et al., 1973; Heckrodt and Bühmann, 1987; Middleburg et al., 1988; Weaver, 1989). In contrast, soils and mudrocks tend to preserve the signatures of the parent rock for low-solubility trace elements, even under intense weathering conditions (Balashov et al., 1964; Cullers et al., 1975; Aubert and Pinta, 1977; Nesbitt, 1979; Davies, 1980; Cullers et al., 1987; Marsh, 1991).

As discussed previously, interstitial cations are removed from clay minerals as weathering proceeds. The rate of release varies as a function of the chemical stability of the host mineral, and the rate of removal in solution varies as a function of the aqueous solubility of the ions involved; but in general, weathered clays evolve towards lower ICV values. Because

of the interstitial cation loss experienced by weathered clays, a very large volume of first-cycle detritus is required to offset the effects of weathering and transport on recycled material. Qualitative calculations show that mudrocks can absorb a significant volume (up to about 25%) of first-cycle material and still show major element trends that reflect net cation loss due to weathering. The low-solubility trace elements on the other hand are not prone to removal in solution, and so their concentrations in a sediment are unlikely to change much as a consequence of weathering. Consequently, their abundance may be noticeably affected by volumetrically minor first-cycle input.

These results confirm the usefulness of trace elements in studies that are concerned with basement composition. They also indicate that trace element compositions of mudrocks are quite sensitive to variations in local or regional basement

Table 4. Rare earth element concentrations in ppm for Colorado Province mudrocks

Sequence	Sample	R	Loc.*	La	Ce	Sm	Eu	Tb	Yb	Lu	ΣREE
Ash Creek	AC.J.139.1	0	1	13.7	31.2	3.6	0.9	0.7	3.9	0.6	56
Yavapai	Y.MC.523	0	3	27.1	55.9	4.5	1.2	0.5	1.4	0.2	94
Yavapai	Y.MC.524	0	3	30.2	63.4	5.6	1.3	0.6	1.6	0.3	106
Yavapai	Y.MC.525	0	3	36.3	71.2	6.8	1.6	0.7	2.2	0.4	122
Yavapai	Y.MC.526	0	3	29.0	76.4	5.5	1.3	0.4	0.9	0.2	117
<b>MEDIAN</b>				<b>29.0</b>	<b>63.4</b>	<b>5.5</b>	<b>1.3</b>	<b>0.6</b>	<b>1.6</b>	<b>0.3</b>	<b>106</b>
Texas Gulch	TG.PR.156.1	1	6	16.3	44.3	3.1	0.6	0.4	1.4	0.3	73
Texas Gulch	TG.PR.156.3	1	6	18.1	35.8	3.0	0.7	0.3	1.4	0.3	67
Texas Gulch	TG.PR.157	1	6	9.0	22.0	2.1	0.5	0.3	1.4	0.2	42
Texas Gulch	TG.PR.158	1	6	9.7	0.0	2.0	0.7	0.4	1.6	0.3	22
Texas Gulch	TG.M.164	1	7	17.9	59.3	3.4	0.7	0.4	2.2	0.4	92
Alder	COX.202	1	4	34.2	74.8	5.0	1.1	0.6	2.1	0.4	123
Alder	COX.203.2	1	4	40.4	71.3	6.4	1.3	0.7	2.3	0.4	129
Alder	COX.205	1	4	36.9	64.7	4.0	0.8	0.4	1.4	0.3	112
Vallecito	V.DHC.278	1	13	4.8	12.4	1.7	0.6	0.5	3.2	0.5	38
Vallecito	V.DHC.280	1	13	10.5	19.8	3.2	1.0	0.5	2.0	0.3	51
Vadito	V.PF.431	1	9	47.8	102.0	12.0	2.5	2.0	7.5	1.1	185
Vadito	V.PF.432	1	9	34.0	62.0	9.6	2.3	1.7	7.0	1.0	128
Vadito	V.PF.434	1	9	28.4	52.9	9.5	2.3	1.7	7.6	1.1	114
Alder	ALTC.518	1	4	35.3	72.2	10.0	2.9	1.6	5.2	0.9	133
Alder	ALTC.519	1	4	46.0	89.0	8.4	1.5	0.8	2.8	0.5	154
Alder	ALTC.520	1	4	42.2	81.5	7.5	1.4	0.8	2.9	0.5	142
Alder	ALTC.522	1	4	28.2	58.2	5.7	1.3	0.8	2.7	0.4	102
Alder	A.Y.651	1	5	37.2	58.2	7.2	1.2	0.7	3.1	0.5	114
Alder	A.Y.652	1	5	42.9	59.5	6.8	1.4	0.8	2.9	0.5	121
Alder	A.Y.653	1	5	45.3	88.4	7.5	1.6	0.8	3.4	0.5	153
Alder	A.Y.655	1	5	21.9	46.4	4.7	0.9	0.6	3.0	0.6	84
Alder	A.Y.658	1	5	35.4	41.5	6.4	1.3	0.9	3.1	0.6	96
Alder	A.Y.659	1	5	36.4	61.6	6.8	1.3	0.7	3.5	0.6	117
Alder	A.Y.660	1	5	53.8	107.0	9.9	1.8	1.1	3.6	0.7	184
<b>MEDIAN</b>				<b>34.8</b>	<b>59.4</b>	<b>6.4</b>	<b>1.3</b>	<b>0.7</b>	<b>2.9</b>	<b>0.5</b>	<b>113</b>
Uncompaghe	BC-4UF**	2		56.0	105.0	11.0	1.8	1.3	4.6	0.8	182
Uncompaghe	BC-5UF**	2		45.7	94.0	8.9	1.4	0.9	4.2	0.7	158
Hondo	O.PS.127.1	2	11	23.0	35.1	2.4	0.4	0.3	1.5	0.3	76
Hondo	O.PS.127.2	2	11	20.7	37.1	2.1	0.3	0.2	1.2	0.2	75
Mazatzal	M.P.153	2	18	291.0	500.0	52.0	9.1	6.9	20.9	3.0	903
Mazatzal	M.TB.174	2	16	94.7	189.0	17.7	3.7	2.6	8.1	1.1	335
Hess Canyon	WL.YJ.181.2	2	17	46.6	111.0	8.1	1.5	1.2	3.5	0.6	192
Hess Canyon	WL.YJ.182	2	17	32.6	62.0	6.3	1.3	1.0	4.6	0.8	128
Hess Canyon	WL.YJ.185	2	17	35.3	87.8	9.8	1.9	1.6	5.4	0.8	162
Hess Canyon	BJ.BJ.190	2	17	15.7	29.1	3.6	0.7	0.6	3.3	0.6	73
Mazatzal	MS.BC.193	2	14	41.6	81.6	7.1	1.2	0.9	3.7	0.5	153
Mazatzal	MS.BC.194	2	14	48.3	100.0	7.9	1.5	0.9	3.4	0.6	179
Mazatzal	COX.210	2	14	44.8	86.1	8.4	1.3	1.2	5.2	0.7	164
Uncompaghe	U.LC.288	2	19	79.5	137.0	11.7	2.3	1.1	5.5	1.0	259
Uncompaghe	U.LC.290	2	19	47.0	96.4	9.4	1.7	1.2	5.8	0.9	183
Uncompaghe	U.LC.291	2	19	23.4	46.5	4.6	0.8	0.7	3.5	0.6	101
Mazatzal	M.P.361	2	18	60.9	95.4	6.9	1.4	0.7	3.5	0.6	189
Mazatzal	MS.STC.436	2	15	55.4	96.5	9.8	1.6	1.1	3.8	0.6	188
Mazatzal	MS.STC.438	2	15	54.5	84.5	8.9	1.6	1.0	3.8	0.6	172
Mazatzal	MS.STC.440	2	15	47.4	98.3	8.8	1.4	1.2	5.1	0.8	180
Mazatzal	MS.STC.441	2	15	54.9	112.0	10.0	1.7	1.1	4.2	0.6	202
Mazatzal	DM.STC.442	2	15	46.5	81.9	11.5	2.2	1.8	5.6	0.8	167
Mazatzal	DM.STC.443	2	15	51.1	99.0	10.9	2.1	1.5	6.0	0.9	189
Mazatzal	MS.DC.448	2	14	79.4	161.0	16.5	2.7	1.8	6.8	1.1	285
Mazatzal	D.R.821	2	18	46.0	87.0	7.8	1.4	0.8	2.7	0.4	166
<b>MEDIAN</b>				<b>47.0</b>	<b>95.4</b>	<b>8.9</b>	<b>1.5</b>	<b>1.1</b>	<b>4.2</b>	<b>0.7</b>	<b>178</b>

composition, and may potentially be used as provenance indicators for cratonic sedimentary sequences.

## 6. SYNTHESIS

The progressive evolution in the average composition of samples through time implies a first-order control on mudrock chemistry. There are two possible first-order controls on mudrock composition: (1) evolution of the composition of the exposed crystalline upper crust; and (2) progressive weathering of sedimentary material over a series of recycling events. Both processes have been active in the history of the Colorado Province.

(1) Evolution of upper crustal composition in the Colorado Province is evident from Fig. 3, which shows that the earliest continental crust in the Colorado Province had a high proportion of mafic and intermediate rocks, but that subsequent additions were overwhelmingly granitic (Reed et al., 1987; Bickford, 1988). The slope of the curve is a function of the rate of addition of granitic material to the crust, but not necessarily the rate at which that change would be evident in the sedimentary record. There is a variable lag time between the crystallisation of igneous rock and its exposure at the surface, and therefore the rate of increase of the granitic component of sedimentary source rocks is probably somewhat lower.



Table 4 Continued

Sequence	Sample	R	Loc*	La	Ce	Sm	Eu	Tb	Yb	Lu	ΣREE
Apache	Ap.YR.470	3	25	57.7	119.0	9.5	1.5	1.0	3.9	0.6	221
Apache	Ap.RD.514	3	27	40.3	91.4	9.5	1.6	1.3	4.5	0.7	179
Grand Canyon S.	H.MC.536	3	22	15.0	37.6	7.2	1.2	0.7	3.1	0.5	90
Grand Canyon S.	H.MC.536	3	22	19.6	42.0	4.7	0.9	0.7	2.8	0.4	96
Grand Canyon S.	S.C.545	3	22A	41.8	83.0	7.9	1.1	0.6	2.9	0.5	141
Grand Canyon S.	H.TT.555b	3	22A	30.3	65.9	7.1	0.9	1.0	4.2	0.6	113
Grand Canyon S.	H.TT.558b	3	22A	26.3	58.5	6.9	1.2	1.1	4.2	0.6	102
Grand Canyon S.	H.TT.562	3	22A	30.9	58.8	7.0	1.5	1.0	3.5	0.5	106
Grand Canyon S.	H.TT.563	3	22A	35.1	68.0	12.3	2.4	1.2	3.0	0.5	125
Grand Canyon S.	H.TT.564	3	22A	16.8	95.9	33.6	7.8	7.4	8.7	1.0	174
Grand Canyon S.	H.TT.577b	3	22A	24.0	49.6	5.7	1.1	0.7	3.0	0.5	88
Grand Canyon S.	H.PC.578b	3	23	30.2	57.9	6.8	1.1	0.9	3.7	0.6	127
Grand Canyon S.	H.PC.583b	3	23	47.2	90.7	8.2	1.4	1.1	4.8	0.7	180
Grand Canyon S.	H.PC.586	3	23	31.8	61.4	7.0	1.2	1.2	3.4	0.6	133
<b>MEDIAN</b>				<b>30.6</b>	<b>63.7</b>	<b>7.1</b>	<b>1.2</b>	<b>1.0</b>	<b>3.6</b>	<b>0.6</b>	<b>126</b>
Ignacio	I.LC.254	4	40	44.3	92.0	5.1	0.8	0.8	5.6	0.9	193
Tapeats	T.J.365	4	28	103.0	222.0	18.5	2.7	2.4	10.7	1.6	393
Bright Angel	BA.PB.377	4	37	94.6	182.0	11.2	1.7	1.2	6.0	0.9	339
Bright Angel	BA.MC.531	4	38	90.3	198.0	9.8	1.3	0.8	5.6	0.9	349
Bright Angel	BA.MC.532	4	38	71.9	113.0	8.7	1.2	0.8	4.1	0.6	242
Bright Angel	BA.MC.633	4	38	60.0	124.0	9.9	1.5	1.1	5.0	0.8	244
Bright Angel	BA.PC.625	4	37	71.8	136.0	9.7	1.3	1.0	5.1	0.8	267
Bright Angel	BA.PC.626	4	37	70.1	129.0	8.5	1.4	1.0	5.1	0.8	257
Bright Angel	BA.PC.627	4	37	61.1	118.0	8.0	1.1	0.8	5.2	0.8	236
Bright Angel	BA.PC.628	4	37	54.7	123.0	7.5	1.1	0.7	4.6	0.7	233
Bright Angel	BA.PC.630	4	37	67.9	128.0	9.5	1.4	1.2	5.7	0.9	256
Bright Angel	BA.PC.631	4	37	81.2	164.0	8.8	1.2	0.9	4.9	0.8	303
Bright Angel	BA.PC.633	4	37	80.7	169.8	9.8	1.4	1.7	8.7	1.2	314
Bright Angel	BA.PC.634	4	37	63.3	116.0	7.9	1.2	0.9	5.5	0.8	237
Bright Angel	BA.TT.635	4	37	67.1	117.1	9.3	1.3	0.9	5.2	0.8	243
Bright Angel	BA.PC.637	4	37	60.1	133.0	12.2	1.8	2.2	9.1	1.1	261
Tapeats	T.GC.636	4	31	61.0	141.0	10.6	1.8	1.4	8.6	1.2	281
Tapeats	T.GC.639	4	31	80.0	163.0	15.3	2.5	1.8	6.8	1.0	305
<b>MEDIAN</b>				<b>69.0</b>	<b>131.0</b>	<b>9.6</b>	<b>1.3</b>	<b>1.0</b>	<b>5.5</b>	<b>0.9</b>	<b>258</b>
Dakota	M.PR.329	5	48	33.7	62.4	5.4	1.0	0.6	2.5	0.4	159
Dakota	D.FC.217	5	42	40.4	73.0	6.8	1.1	1.0	4.3	0.7	174
Dakota	D.FC.224	5	42	39.9	71.4	7.0	1.1	0.8	3.2	0.6	171
Dakota	D.TC.226A	5	43	33.8	60.1	5.2	0.8	0.4	2.1	0.3	151
Dakota	D.AR.239	5	44	31.5	60.3	5.7	1.0	0.7	2.6	0.4	151
Dakota	D.FC.250	5	42	32.8	57.8	7.1	1.0	0.7	3.0	0.6	150
Dakota	D.BM.314	5	45	28.5	57.2	5.2	0.8	0.5	2.6	0.4	145
Dakota	D.CB.337	5	46	39.7	76.5	6.7	1.1	0.7	3.1	0.5	179
Dakota	D.CS.420	5	46	61.1	121.0	10.0	1.6	1.2	5.4	0.8	252
Dakota	D.CS.421	5	46	38.9	73.6	7.1	1.1	0.8	3.2	0.5	176
<b>MEDIAN</b>				<b>36.4</b>	<b>66.9</b>	<b>6.7</b>	<b>1.0</b>	<b>0.7</b>	<b>3.0</b>	<b>0.5</b>	<b>164</b>
<b>p value</b>				.2319	.1803	.8470	.2399	.8505	.4664	.4358	.2322

\* Locality numbers keyed to Fig. 4 and to localities in Cox (1993)

\*\* Samples provided by D.A. Gonzales

(2) Recycling of older sedimentary rocks was significant in the Colorado Province because, subsequent to the orogenic events which accompanied crustal accretion (Fig. 2), deformation in the Colorado Province was dominated by vertical movements, mainly arching and block faulting (Keith and Wilt, 1986; Baars et al., 1988; Sloss, 1988), which were rarely sufficient to completely strip the sedimentary cover and expose basement on a regional scale. Evidence that much of the sediment in each of the Colorado Province sedimentation intervals subsequent to R1 was derived by recycling of older sedimentary sequences is provided by the increasing abundance of sedimentary clasts in conglomerates, and by the composition of associated sandstones (Cox, 1993; Cox and Lowe, 1995b). Colorado Province sandstones also record a progressive increase in compositional maturity, due to a com-

bination of protracted weathering of sedimentary detritus during multiple recycling episodes and decreasing average input of basement-derived detritus to the sedimentary system (Cox and Lowe, 1995b).

The major element chemistry of the Colorado Province mudrocks, which indicates a general increase in the proportion of clay minerals at the expense of nonclay silicate minerals, reflects increasing average compositional maturity of the sediment mass. In addition, the examination of the ICV and the  $K_2O/Al_2O_3$  ratio demonstrate that early mudrocks contained little K-feldspar whereas later nonclay silicate additions to mudrocks were dominated by K-feldspar. Trace element distributions indicate that an increasing proportion of fractionated igneous material was being input to the sedimentary system over time. These observations are consistent with

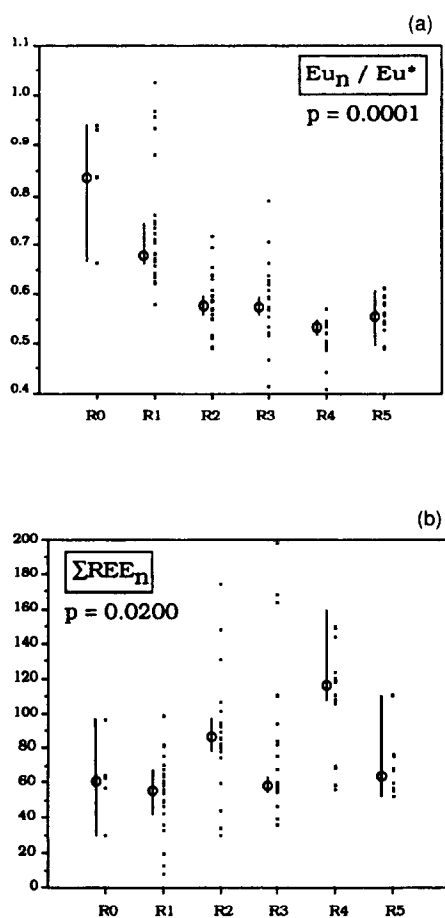


FIG. 12. Graphs of REE data as a function of sedimentation interval. For explanation of  $p$  statistic, see caption to Fig. 7. Dots represent data points; circles represent group medians. Bars represent 94–98% confidence intervals about the averages. Subscript  $n$  denotes data normalised to chondrites: normalisation factors are from Wakita et al. (1971).  $Eu^*$  is calculated by extrapolating between Sm and Tb on a graph of relative abundance vs. atomic number, and applying the equation for a geometric progression:

$$Eu^* = Tb \cdot \left( \sqrt[3]{Sm/Tb} \right)^2$$

Two data points are not shown on the graphs for reasons of scale: (a) One value in R2:  $\Sigma REE = 900$  ppm; (b) One value in R2:  $\Sigma REE_n = 485$ .

the tectonic evolution of the Colorado Province from a series of accreted arc terranes composed of igneous and metamorphic rocks with a wide range of compositions, including a substantial proportion of mafic material, to a stable craton with a high proportion of granitic upper crustal material and a well-developed sedimentary mantle.

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