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Titanian chromite and chromian titanomagnetite from a Snake River Plain basalt, a terrestrial analogue to lunar spinels

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Abstract

An Upper Pleistocene vitrophyric pillow basalt from the Snake River Plain, southern Idaho, contains a small amount of spinel microphenocrysts. Electron microprobe analyses show that these are continuously zoned with a composition range intermediate between the chromites and titanomagnetites. Their major oxide abundances are: Fe as FeO 46.5–52.1 percent, Cr_2O_3 15.5–22.9 percent TiO_2 7.8–15.1 percent, Al_2O_3 7.2–12.5 percent and MgO 6.3–7.7 percent. The spinels appear to have formed by direct precipitation from basaltic magma and to have been quenched rapidly from a temperature of 1140° C. Their compositions are as close to those of the complex Fe–Ti–Cr–Al spinels in lunar lavas as might be expected at terrestrial volcanic conduit fO_2 levels.

Introduction

Before the advent of electron probe micro-analytical techniques, our knowledge of the chemistry of spinels in basic rocks was largely dependent upon analyses of mineral separates from basic intrusions. These, with very few exceptions (*e.g.,* Frankel, 1942), suggested the presence of a wide miscibility gap between Cr–rich and Ti–rich compositions. Subsequent microprobe studies of both plutonic (*e.g.,* Henderson and Suddaby, 1971: Frisch, 1971) and terrestrial volcanic basaltic spinels (*e.g.,* Evans and Moore, 1968; Gunn, Coy-Yll, Watkins, Abranson, and Nougier, 1970) yielded many analyses of compositions intermediate between the chromites and magnetites. However, these were generally supposed not to have precipitated as such from basaltic magmas but to have formed when early crystallized chromite reacted with interstitial liquid during the final stages of consolidation of the rocks.

The recent spate of microprobe analyses of spinels in lunar lavas, summarized by Haggerty (1971, 1972a, b), has produced many examples of compositions intermediate between chromite and ulvöspinel. There seems to be general agreement among the lunar investigators that, at least in some instances, a complete range from Cr–rich to Ti–rich spinels precipitated from lunar magmas. The description and discussion of a comparable terrestrial occurrence is presented here.

Occurrence

A thick Pliocene-to-Recent fissure-erupted lava pile underlies the Snake River Plain of southern Idaho. The lavas are almost all tholeiitic, varying from Mg–rich olivine tholeiites to Fe–rich tholeiitic andesites (Powers, 1960: Tilley and Thompson, 1970). The author has used several samples of these lavas as starting materials for experimental studies (Thompson, 1972a, b) and has determined their mineralogy with the electron microprobe as part of this work. One specimen is a pillow lava from the Upper Pleistocene Bancroft Springs Basalt in the Snake River Group (Malde and Powers, 1962). It is extremely fresh for a pre-historic terrestrial lava, consisting of olivine and plagioclase phenocrysts and sparse spinel microphenocrysts in a clear brown glass. The composition of the lava (Table 1) places it at the iron and alkali-rich end of the basalt range. Its Cr content has been determined by G. D. Borley, using X-ray fluorescence spectrometry with W-1 as standard. A value of 195 ppm was obtained.

The phenocrysts are all euhedral. Plagioclase is elongate, up to 6 mm in length, and zoned from An_{65} cores to An_{59} rims. Olivine is equant, up to 2 mm in length, and zoned from Fo_{73} cores to Fo_{69} rims. The spinels range from 10 to 130 μm. They occur within the olivine phenocrysts, protruding from them into the glass, or wholly within the glass. Occasional spinel crystals are found in the plagioclase pheno-

TABLE 1. Chemical Analyses and CIPW Norms of Snake River Plain Basalt and its Interstitial Glass

	1	2		1	2
SiO_2	47.76	47.99	or	4.45	5.56
TiO_2	3.03	3.99	ab	22.01	22.53
Al_2O_3	14.93	13.24	an	26.69	21.13
Fe_2O_3	1.36	1.61	di	13.57	18.31
FeO	12.37	13.60	hy	15.49	18.33
MnO	0.20	0.23	ol	8.37	2.41
MgO	6.70	5.32	ilm	5.78	7.61
CaO	9.41	9.56	mt	2.09	2.32
Na_2O	2.62	2.64	ap	1.34	1.68
K_2O	0.75	0.91	rest	0.04	0.05
H_2O^+	NIL	0.03		99.83	99.93
H_2O^-	0.03	0.02			
P_2O_5	0.53	0.69			
CO_2	0.01	NIL			
	99.70	99.83			

1. *Bancroft Springs Basalt, Snake River Group, mouth of Malad River, Gooding Co., Idaho. Field no. 59-P-13. Analyst D.F. Powers, U.S.G.S. (Tilley and Thompson, 1970, Table 1).*
2. *Glass separated from 59-P-13. Analyst D.F. Powers, U.S.G.S. (Tilley and Thompson, 1970, Table 1).*

crysts. The calculated mode of the specimen (Bryan, Finger, and Chayes, 1969) is 7.4 percent olivine, 14.9 percent plagioclase and 77.7 percent glass. The amount of spinel, considerably below one percent, is too low to be estimated accurately by either calculation or point-counting of the single thin section available. The thinnest edges of spinels in the centers of olivine phenocrysts transmit a very small amount of light. Otherwise the mineral is opaque.

Spinel Chemistry

The analyses were made with the computer-automated MAC model 400 electron microprobe of the Geophysical Laboratory (Finger and Hadidiacos, 1971). The accelerating potential was 15 kV, the specimen current 0.12 μa and the integration time on the scalers 30 seconds. The standards used were chromite for Cr, Mg, and Al; aenigmatite for Fe, Ti, and Si; a Mn-doped glass near pyrope in composition for Mn; and a glass of diopside composition for Ca (Boyd, 1968). Raw data were corrected by the method of Bence and Albee (1968) and are thought to be accurate to ±2 percent for major elements and ±5 percent or more for minor elements.

All the spinel crystals show slight continuous zoning, from Cr-rich cores to Cr-poor rims. The spinels in the cores of olivine phenocrysts have the highest overall Cr contents. Intermediate Cr values are found in crystals protruding from olivines, and spinels wholly within glass are the poorest in Cr. The chemical data are summarized in Figure 1, and representative analyses are given in Table 2; the remainder may be obtained from the author.

Figure 1 shows that Fe is correlated positively, and Cr, Al and Mg negatively with Ti in these spinels. Ca is below detection limit in the Ti-poor compositions but rises sharply in the most Ti-rich analyses. Mn and Si remain approximately constant throughout the series (Table 2). The bi-modal distribution of points on Figure 1 is thought to be a result of sampling bias when points were being chosen for analysis. Distinctively Cr-rich or Cr-poor crystals were searched for, in order to define the full extent of chemical variation in the specimen.

Mg and Al occur in substantial amounts in these spinels and show systematic variation (Fig. 1). Thus, their compositions are considerably more complex than simple binary solid solutions between chromite

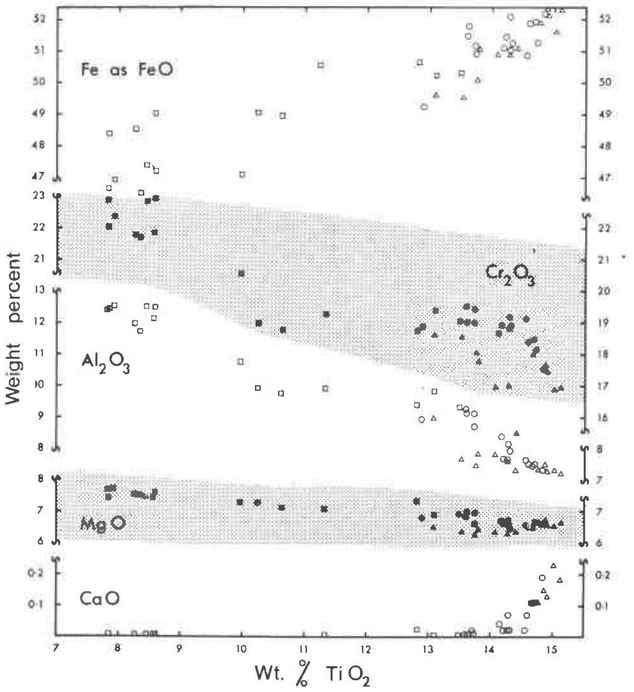

FIG. 1. Compositional trends among spinels in Snake River basalt 59-P-13. An example of the extent of zoning within individual crystals is given in Table 2. The symbols distinguish the petrographic locations of the spinels thus: square = inside olivine phenocryst, circle = protruding from olivine phenocryst, triangle = in glass.

TABLE 2. Representative Selection of Electron Probe Analyses of Spinel Microphenocrysts in a Snake River Plain Basalt, 59-P-13

	1 Ol	2 Ol	3 Ol	4 Ol	5 Gl	6 Gl	7 O/G	8 O/G	9 Gl	10 Gl
SiO_2	0.30	0.20	0.37	0.21	0.22	0.37	0.19	0.19	0.30	0.27
TiO_2	7.84	8.27	9.97	11.3	13.1	13.8	14.3	14.6	15.0	15.1
Al_2O_3	12.4	12.0	10.8	9.91	8.95	7.85	7.97	7.63	7.32	7.20
Cr_2O_3	22.9	21.8	20.6	19.3	18.6	17.8	18.9	19.1	16.9	17.0
Fe_2O_3	19.6	21.0	18.1	19.8	16.6	17.4	16.7	16.3	17.1	17.7
FeO	29.0	29.7	30.8	32.8	34.6	35.4	36.2	36.2	36.2	36.4
MnO	0.36	0.32	0.41	0.38	0.41	0.42	0.39	0.38	0.40	0.43
MgO	7.68	7.52	7.31	7.07	6.46	6.43	6.46	6.55	6.52	6.64
CaO	0.00	0.00	0.00	0.00	0.02	0.02	0.02	0.02	0.23	0.18
	100.0	100.7	98.3	100.7	99.0	99.4	101.1	100.9	100.0	100.9
ATOMIC PROPORTIONS BASED ON O=32										
Si	0.079	0.047	0.097	0.055	0.057	0.097	0.048	0.048	0.081	0.072
Ti	1.572	1.656	2.056	2.301	2.721	2.871	2.929	2.986	3.110	3.109
Al	3.916	3.775	3.483	3.159	2.916	2.562	2.561	2.456	2.381	2.322
Cr	4.844	4.599	4.467	4.111	4.069	3.887	4.073	4.125	3.685	3.672
Fe^{3+}	3.942	4.226	3.748	4.022	3.466	3.622	3.416	3.356	3.556	3.646
Fe^{2+}	6.501	6.636	7.066	7.414	8.018	8.211	8.260	8.274	8.351	8.326
Mn	0.079	0.070	0.088	0.087	0.089	0.097	0.088	0.088	0.089	0.096
Mg	3.066	2.990	2.992	2.849	2.664	2.651	2.625	2.665	2.681	2.708
Ca	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.064	0.048

Notes: 1. Petrographic relations of each points are indicated at the head of the columns thus: Ol=within olivine phenocryst, O/G= protruding from olivine, Gl=within glass.

2. Points 7 and 8 are core and margin respectively of a single microphenocryst, indicating the typical extent of zoning.

3. FeO, Fe_2O_3 and oxide sums are calculated by assuming spinel R_3O_4 stoichiometry.

and titanomagnetite. In this they resemble lunar spinels (Haggerty, 1972a, b). A minimum of six variables—Cr, Al, Mg, Ti, Fe^{2+} and Fe^{3+}—would have to be plotted on a diagram in order to summarize successfully the range of chemical compositions of Snake River spinels relative to other occurrences of this mineral. Even a Johnstone spinel prism (Stevens, 1944) cannot encompass this complexity. The number of components has therefore been reduced to four in Figure 2 by eliminating Mg and the variable valency of Fe. The close positive correlation between Mg and Al (Fig. 1) allows Mg in these spinels to be monitored by plotting their Al variation. As Fe^{2+} and Fe^{3+} can only be allocated by charge balance calculations, it seems illogical to consider them at the expense of independently measured elements.

Within the limitations just noted, Figure 2 relates the chemistry of the Snake River spinels to other volcanic terrestrial and lunar examples. If the complete set of lunar data are plotted (Haggerty, 1972a, b), the series from Al- (and Mg-) rich chromites to ulvöspinel is continuous. Previously-published terrestrial chromian titanomagnetite analyses fall much nearer the Fe composition point on Figure 2 than do their lunar counterparts because they contain substantial amounts of Fe^{3+} and relatively little Al. The new Snake River analyses presented here occupy an intermediate position on Figure 2 between the lunar chromian ulvöspinels and other terrestrial chromian titanomagnetites. They are thus a new compositional variant in the chemical complexities of volcanic spinels.

Discussion

The authors of previous descriptions of terrestrial spinels intermediate between chromite and the magnetite-ulvöspinel series have all favored the hypothesis that these compositions form by post-precipitation alteration of chromite. Frequently there is strong evidence to support this idea. Thus the boundary between Cr-rich and Ti-rich spinel in a zoned crystal may be sharp, rather than gradational (Gunn *et al*, 1970). Similarly, in the prehistoric Makaopuhi lava lake, Hawaii (Evans and Moore, 1968), the most Cr-rich spinels are in the chilled uppermost basalt, whereas progressively more Ti-rich compositions occur in the deeper more slowly cooled parts of the mass. In contrast, there seems to be a consensus of opinion among the investigators of lunar lavas (*e.g.*, Haggerty, 1972a) that most of the intermediate Fe–Ti–Cr spinels in these rocks precipitated as such from magmas.

The Snake River spinels show several features which support a view that they have crystallized directly from a basaltic melt, without significant later modification. First, the crystals show continuous zoning. Second, the overall composition of each crystal correlates well with its inferred position in the crystallization sequence of the rock, as noted above. Third, enough is known about the thermal history of this lava to place severe limits on the amount of post-precipitation change that could have affected the spinels.

Both the lava and its interstitial glass were subjected to one-atmosphere melting studies by Tilley and Thompson (1970). The liquidi of the whole rock and glass are at 1182°C and 1141°C respectively (Tilley and Thompson, 1970, Table 7). The glassy part of the thin section containing the analyzed spinels contains about one percent or less of tiny skeletal and dendritic microlites of olivine, plagioclase and spinel. Little is known about the rates of crystal growth in basaltic magmas. However, it is common experimental experience (the quench-phase problem) that basaltic melts will crystallize extremely rapidly in appropriate circumstances. It therefore seems very unlikely that this Snake River basalt could have taken more than a few minutes to cool from 1140°C to around 950°C, when the viscosity of the liquid would reach values high enough to prevent significant crystal growth.

The proposal that the original chemistry of the Snake River spinels has been preserved by rapid quenching of their host rock receives support from the results of a recent study of chromite in basalts from Kilauea volcano, Hawaii, by Evans and Wright (1972). These authors show that the well defined inter-element chemical trends which characterize the chromites in air-quenched basaltic pumices are not present in samples taken from the surfaces of lava lakes. If rapid quenching to a vitrophyre is necessary to preserve the "primary" pre- or syn-eruption chemistry of spinel microphenocrysts in basalts, it follows that microprobe investigations of such spinels in holocrystalline terrestrial lavas are unlikely to yield much useful information on the compositions of these minerals at the time they were precipitated.

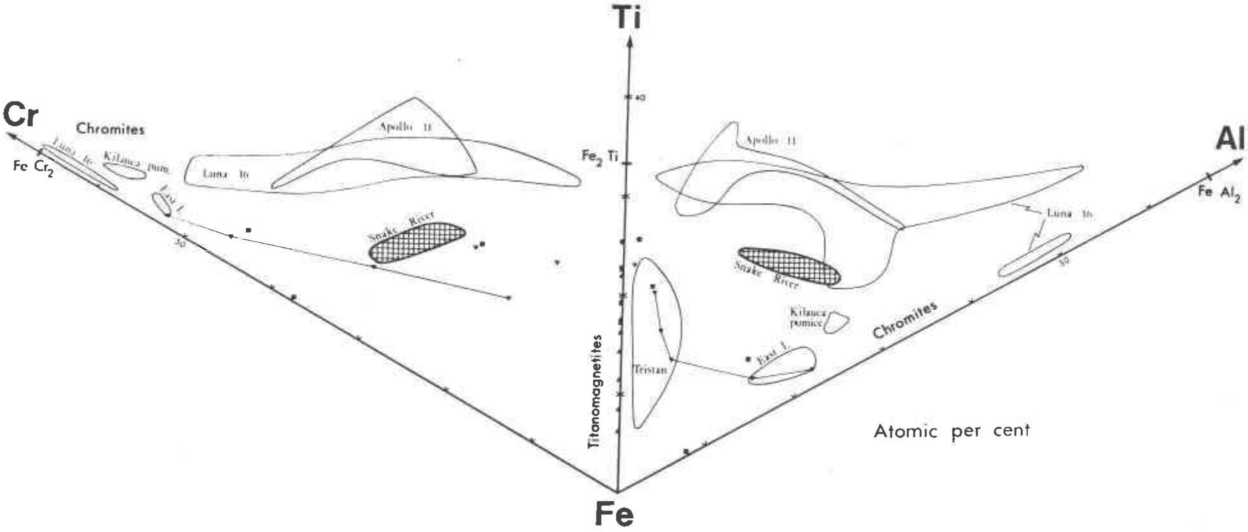

FIG. 2. Variation in Fe, Ti, Al, and Cr among Snake River basalt 59-P-13 spinels and other terrestrial and lunar occurrences of this phase. The diagram is constructed from two ternary atomic plots, Fe-Ti-Cr and Fe-Ti-Al, oriented to share their Fe-Ti sides. All data points and compositional fields appear twice, once in each triangle. ● = Skye, N. W. Scotland; ▲ = Tristan da Cunha, S. Atlantic; ▼ = East Island, Crozet, Indian Ocean; ▼——▼ = Zoned crystal; ■ = Prehistoric Makaopuhi Lava Lake, Hawaii. Sources of the data are Agrell *et al* (1970), Anderson (1968), Evans and Moore (1968), Evans and Wright (1972), Gunn *et al* (1970), Haggerty (1972a), and Thompson (unpublished).

Conversely, the apparent preservation of "primary" spinels in holocrystalline lunar lavas provides further confirmation of the hypothesis put forward by many investigators (*e.g.*, Weill *et al*, 1970) that these rocks crystallized extremely rapidly.

Haggerty (1972b) has pointed out that the aluminous nature of the lunar titanian chromites and chromian ulvöspinels is surprising, because experimental studies of the system Fe_2TiO_4–$FeAl_2O_4$–$FeCr_2O_4$ by Muan, Hauck, and Lofall (1972) indicate that high Al contents should diminish the probability of spinels intermediate between $FeCr_2O_4$ and Fe_2TiO_4 crystallizing from a melt. The Snake River spinels share this paradox, although of course it must be remembered that their Fe^{3+} contents reduce the relevance of any comparison with the work of Muan *et al* (1972). It may be significant that all the reported volcanic occurrences of these unusual compositions appear to be in zoned crystals associated with zoned silicates. If conditions of rapid crystal growth prevailed during the formation of the zoned complex spinels, it is quite possible that their compositions represent metastable equilibrium. Perhaps their Al contents are at least partially functions of crystal growth rates.

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