

1 **HIGHLIGHTS AND REAKTHROUGHS**

2 **MINERALOGICAL SOCIETY of AMERICA**

3 **“Spinel in Planetary Systems.”**

4 **Stephen E. Haggerty**

5 Geology & Environment, Florida International University, Miami 33155.

6 [haggerty@fiu.edu](mailto:haggerty@fiu.edu) In Press 20th April 2015

7 **Abstract:** Spinel is ubiquitous as a rock-forming mineral in terrestrial, lunar and planetary  
8 basalts and closely associated meteoritic equivalents. A major unknown is whether these rocks  
9 formed under similar conditions of partial melting of primary or modified mantle, whether  
10 redox environments played a role in evolutionary trends, and did mineral crystal chemistry  
11 have any influence on elemental partition between solids and liquids? In a novel approach by  
12 Papike et al. (2015), spinel is used as an informative, albeit complex indicator of oxygen  
13 fugacity, site occupancy of multiple valence elements, and spinel structural types. Planetary  
14 basalts may be reduced (IW-3), oxidized (Earth at FMQ), or of intermediate redox state (Mars).  
15 Taking an expansive view, the spinel approach holds enormous promise in understanding the  
16 magmatic differentiation of asteroids.

17 **Spinel:** Latin *spina*- spine [or thorn in allusion to the sharp-edged skeletal form of quenched crystals in  
18 basalts and slags (Haggerty, 1976)]. **Spinel:** Among the first minerals to be examined by X-ray analytical  
19 techniques (Bragg, 1915a, b), preceded by another cubic mineral, diamond in 1913. **Spinel:** Solid  
20 solution members (chromite to ulvöspinel-magnetite) and ilmenite form the *unheralded* oxide third arm  
21 to Bowen’s magmatic silicate crystallization series of olivine to quartz, and anorthite to albite. **Spinel:** In  
22 association with ilmenite solid solutions was the first experimentally determined temperature and  
23 oxygen geobarometer ( $fO_2$ ) (Lindsley, 1976) to show, on application to igneous rocks across the silica  
24 spectra, that basalts and gabbro indeed formed at higher T and lower  $fO_2$  than corresponding rhyolite  
25 and granite that crystallized at lower T and higher  $fO_2$  (Buddington and Lindsley, 1964). **Spinel:** In  
26 structurally transformed olivine (ringwoodite), demarcates the boundary between the upper and lower  
27 mantles in Earth.

28 With classic papers by Irvine “*Chromian spinel as a petrogenetic indicator.*” (Part 1 Theory, 1965; Part 2  
29 Petrologic applications, 1967), and the experimental study by Hill and Roeder on: “*The crystallization of*  
30 *basalt as a function of oxygen fugacity.*” (1974), let’s fast forward to the latest study of the spinel  
31 mineral group in martian basalts. Forward, not side-stepping, but incorporating the important  
32 contributions in the NASA initiative: “*Basaltic Volcanism Study Project: Basaltic Volcanism on the*  
33 *Terrestrial Planets*” (1981), that really set the stage for the use of minerals in solid solution and  
34 crystallization trends to interpret the origin and environmental conditions of rock formation in remote  
35 planets (see extended listing in Papike et al., 2015, who was a Team Leader and who has made  
36 significant contributions to the interpretation of planetary materials.)

37 What’s new in this breakthrough? Firstly is the introduction of vanadium as an additional indicator of  $fO_2$   
38 which is relevant given that solid solution end members are possible and that multiple valence states

39 ( $V^{2+}$  and  $V^{3+}$  for example) exist. Secondly, is the site distribution of valence species with crystallization,  
40 coexisting structural-transformations and oxygen fugacity. To appreciate these nuances it is important  
41 to understand that site-occupancy in the spinel mineral group varies with temperature,  $fO_2$ , and with  
42 crystallization as follows:

43 **NORMAL\* CLASSIC SPINEL:**  $(R^{2+})_8 [R^{3+}]_8 O_{32}$ : where divalent ions are in (tetrahedral) co-ordination and  
44 trivalent are exclusively in [octahedral] co-ordination. Examples are Spinel *sensu stricto* ( $FeAl_2O_4$ );  
45 chromite ( $FeCr_2O_4$ ); picrochromite ( $MgCr_2O_4$ ); and hercynite ( $FeAl_2O_4$ ). Solid solution among these  
46 endmembers is accomplished by simple ionic substitution: Fe for Mg, and Al for Cr.

47 **INVERSE SPINEL:**  $(R^{2+})_8 [R^{2+} Ti^{4+}]_8 O_{32}$ : where a single valence type is split between (tetrahedral) and  
48 [octahedral] co-ordination as in ulvöspinel, and in magnetite where: ferric iron is split between vi and vii  
49 sites as in:  $(Fe^{3+})_8 [Fe^{3+} Fe^{2+}]_8 O_{32}$ . Other examples are quadilite,  $Mg_2TiO_4$ , magnesioferrite,  $MgFe_2O_4$ ,  
50 and coulsonite  $FeV_2O_4$  where Fe is divalent and V is trivalent in vi and vii. Solid solution among these  
51 endmembers is achieved by couple substitution:  $2R^{3+}$  for  $R^{2+} + R^{4+}$ .

52 “Classic” spinel crystallizes early and at relatively low  $fO_2$ . With increasing crystallization, there is a  
53 continuum in compositions from high Cr and Mg to increasing concentrations of  $Fe^{2+}$ ,  $Fe^{3+}$ , and  $Ti^{4+}$ ; this  
54 is occupied by a progressive change to the inverse spinel structure and as Papike et al. (2015)  
55 convincingly show  $V^{2+}$  changes to  $V^{3+}$  as  $fO_2$  becomes more oxidizing on cooling. There are  
56 compositional miscibility gaps between “classic” and inverse spinel groups (summarized in Haggerty,  
57 1976); the discontinuity in structural types may not be sharp but “domains” of inverse structure may  
58 persist (*must* as Papike et al. note) in order to accommodate Ti and limited quantities of ferric iron.  
59 Chrome clearly plays an important role as well with implications for V stability and it here that ranges of  
60  $fO_2$  can be estimated. “Classic” spinels are stable at low  $fO_2$  (Iron wüstite IW-1 to IW+3). More  
61 interesting is the conclusion that: With  $fO_2$  above IW+3, ferric iron is greatly increased and with a  
62 concomitant change in spinel composition, domains of inverse spinel, which have a lower free energy  
63 than the “classic” spinel structure, become prevalent (Papike et al.) The author’s go on to note that  $V^{3+}$  is  
64 compatible with  $Cr^{3+}$  in “classic” spinel, but highly charged ions such as  $Ti^{4+}$  and  $V^{4+}$  are weakly  
65 partitioned, constrained by charge balance. Thus a change in composition and or a change in  $fO_2$  may  
66 dictate and or drive an appropriate change in structural state. This, in addition to the presence of  
67 miscibility gaps and the dearth of compositions between “classic” and inverse spinels means that the  
68 current breakthrough is a major step forward but has yet to reach the finish-line in a complete  
69 understanding of the integrated messages recorded in the complex but informative spinel mineral  
70 group.....that will surely come.

71 Papike et al. provide three interesting examples in which their new spinel data may be applied. The first  
72 concludes that planetary environments with highly reduced conditions (IW-1) will be dominated by  
73 “classic” spinel compositions; more oxidizing conditions such as Earth are buffered at FMQ (fayalite-  
74 magnetite-quartz) to FMQ+1; Mars is intermediate at IW+1 to FMQ. The second relates to a range in  
75 isotopic compositions determined for shergottites; although lacking complete V data, the preliminary  
76 conclusion is that the enriched shergottites are intrinsically more oxidized. The third example is by far  
77 the most profound as it deals with the magmatic differentiation of asteroids; this is an exciting frontier  
78 that promises new and informative interpretations ahead. And with their novel approach the authors  
79 are on the ground floor for substantial new breakthroughs. Spinel is clearly reinstated as the noble of  
80 noble oxides.

81 -----  
82 \*There is nothing “*Normal*” about this distribution. And that applies equally to Earth’s geomagnetic  
83 polarity so “*Classic*” is suggested, and indeed is preferred.

---

84 **REFERENCES CITED**

- 85 Basaltic Volcanism Study Project (1981) Basaltic volcanism on the terrestrial planets. Pergamon Press,  
86 1286 pages.
- 87 Bragg, W.H. (1915a) The structure of magnetite and spinels. *Nature*, 95, 561.
- 88 Bragg, W.H (1915b) The structure of the spinel group of crystals. *Philosophical Magazine Series 6*, 30,  
89 305-315.
- 90 Buddington, A. F., and Lindsley, D.H. (1964) Iron titanium oxide minerals and synthetic equivalents.  
91 *Journal of Petrology*, 5, 310-357.
- 92 Haggerty, S.E. (1976) Opaque mineral oxides in terrestrial rocks. In D. Rumble, Ed., *Oxide Minerals*, 3,  
93 Hg-101-Hg-300. *Reviews in Mineralogy*, Mineralogical Society of America, Chantilly, Virginia.
- 94 Hill, R. and Roeder, P. (1974) The crystallization of basaltic liquid as a function of oxygen fugacity. *Journal*  
95 *of Geology*, 82, 709-729.
- 96 Irvine, T. N. (1965) Chromian spinel as a petrogenetic indicator. Part 1 Theory. *Canadian Journal of Earth*  
97 *Science*, 2, 648-672.
- 98 Irvine, T.N. (1967) Chromian spinel as a petrogenetic indicator. Part 2 Petrologic applications. *Canadian*  
99 *Journal of Earth Science*, 4, 71-103.
- 100 Lindsley, D.H. (1976) Experimental studies of oxide minerals. In D. Rumble, Ed., *Oxide Minerals*, 3, L-61 –  
101 L-88. *Reviews in Mineralogy*, Mineralogical Society of America, Chantilly, Virginia.
- 102 Papike, J.J., Burger, P.V., Bell, A.S., Shearer, C.K., Le, L., and Jones, J. (2015) *American Mineralogist*....this  
103 vol.