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13. Geochemical characteristics and isotopes as petrogenetic indicators: a review

Elementi in tracce e isotopi come indicatori petrogenetici



Further Readings: Wilson 1989, chapter Two; Rollinson 1993; Winter 2001.

"La Scienza come arte dell'approssimazione" (Luca Cavalli-Sforza)

 Gli elementi in tracce (<0.1wt %; 1.000 ppm) sono *più sensibili degli elementi maggiori* ai processi di PM, FC, MIX

- le loro concentrazioni possono variare di alcuni ordini grandezza

- la loro *distribuzione* è regolata da *leggi matematiche* che rendono possibile un *approccio quantitativo* alla petrogenesi delle rocce (e.g. Gast, 1968)

Review of trace elements Chemical Fractionation and Distribution Coefficient (K_D)

Coefficiente di Distribuzione

$$K'_{D_s} = \frac{C'_s}{C'_i}$$
 Dove:

C' = Concentrazione dell'elemento i nel solido

C' = Concentrazione dell'elemento *i* nel liquido in equilibrio con quel solido

• Incompatible vs. Compatible element



 Incompatible elements have also been called hygromagmatophile (Treuil and Varet, 1973)

Incompatible elements: two subgroups

 Smaller, highly charged high field strength (HFS) elements (REE, Th, U, Ce, Pb⁴⁺, Zr, Hf, Ti, Nb, Ta)

 Low field strength large ion lithophile (LIL) elements (K, Rb, Cs, Ba, Pb²⁺, Sr, Eu²⁺) are more mobile, particularly if a fluid phase is involved • Sr and Ba (also incompatible elements)

Sr is excluded from most common minerals except plagioclase

▲ Ba similarly excluded except in alkali feldspar

		Olivine	Орх	Срх	Garnet	Plag	Amph	Magnetite		
Rb		0.010	0.022	0.031	0.042	0.071	0.29			
Sr		0.014	0.040	0.060	0.012	1.830	0.46			
Ba		0.010	0.013	0.026	0.023	0.23	0.42			
Ni		14	5	7	0.955	0.01	6.8	29		
Cr		0.70	10	34	1.345	0.01	2.00	7.4		
La		0.007	0.03	0.056	0.001	0.148	0.544	2		
Ce	nts	0.006	0.02	0.092	0.007	0.082	0.843	2		
Nd	ше Ш	0.006	0.03	0.230	0.026	0.055	1.340	2		
Sm	Ē	0.007	0.05	0.445	0.102	0.039	1.804	1		
Eu	긑	0.007	0.05	0.474	0.243	0.1/1.5*	1.557	1		
Dy	Еa	0.013	0.15	0.582	1.940	0.023	2.024	1		
Er	ହ	0.026	0.23	0.583	4.700	0.020	1.740	1.5		
Yb	R B	0.049	0.34	0.542	6.167	0.023	1.642	1.4		
Lu		0.045	0.42	0.506	6.950	0.019	1.563			
Data	Data from Rollinson (1993). * Eu ³⁺ /Eu ²⁺ Italics are estimated									

Table 9-1. Partition Coefficients (C_S/C_L) for Some Commonly Used TraceElements in Basaltic and Andesitic Rocks

Compatible example:

- Ni strongly fractionated -> olivine > pyroxene
- Cr and Sc \rightarrow pyroxenes \gg olivine
- Ni/Cr or Ni/Sc can distinguish the effects of olivine and augite in a partial melt or a suite of rocks produced by fractional crystallization

Table 9-1.	Partition Coefficients (C_S/C_L) for Some Commonly Used Trace
	Elements in Basaltic and Andesitic Rocks

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Ва	0.010	0.013	0.026	0.023	0.23	0.42	
Ni	14	5	7	0.955	0.01	6.8	29
Cr	0.70	10	34	1.345	0.01	2.00	7.4

See Table 9.6 in Appendix

• Incompatible vs. Compatible element

Compatibility and incompatibility depend on minerals and melts involved

Partition coefficients for REE between hbl and basaltic to rhyolitic melts. After Rollinson, 1993)



• For a rock, determine the bulk distribution coefficient D for an element by calculating the contribution for each mineral

$$\mathbf{D}_{i(bulk)} = \mathbf{\Sigma} \mathbf{W}_{A} \mathbf{D}_{iA}$$

 W_A = weight % of mineral A in the rock

 D_{iA} = partition coefficient of element i in mineral A

Calcolo del coefficiente di distribuzione globale D

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Er	are	0.026	0.23	0.583	4.700	0.020	1.740	1.5		
Yb	Ŕ	0.049	0.34	0.542	6.167	0.023	1.642	1.4		
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Esempio: calcolo di D^{Er}_{bulk} in una ipotetica lherzolite a grt costituita da: 60% ol, 25% opx, 10% cpx, e 5% grt, usando i dati di Tab.9.1 $D_{Er} = (0.6 \cdot 0.026) + (0.25 \cdot 0.23) + (0.10 \cdot 0.583) + (0.05 \cdot 4.7) = 0.366$



D_i »1.0 (compatible element) Very low concentration in melt, especially for low % melting (low F) 10 CL/Co Variation in the relative concentration of a trace element in a liquid vs. source rock as a fiunction of D and the fraction melted, using equation for equilibrium 0.1 batch melting (after Winter, 2001)



Highly incompatible elements
Greatly concentrated in the initial small fraction of melt produced by partial melting
Subsequently diluted as F increases

Variation in the relative concentration of a trace element in a liquid vs. source rock as a fiunction of D and the fraction melted, using equation for equilibrium batch melting. From Winter (2001)



Per ogni elemento fortemente incompatibile
$$(D_i \rightarrow 0)$$

$$\frac{C_L}{C_0} = \frac{1}{D_i(1-F)+F} \longrightarrow \frac{C_L}{C_0} = \frac{1}{F}$$

Nell'ipotesi di una fusione parziale di 1%, 3%, 5% (F=0.01/ 0.03/ 0.05) avremmo un fattore d'arricchimento: $C_L/C_0 = 100/33/20$



2. Fractional Crystallization (FC)

Equilibrium Crystallization (EC)

Crystals remain in equilibrium with each melt increment

Rayleigh Fractionation (RFC)

The other extreme: separation of each crystal as it formed=perfectly continuous fractional crystallization in a magma chamber

 Concentration of some element in the *residual* liquid, C_L is modeled by the Rayleigh equation:

$C_L/C_O = F^{(D - 1)}$ Rayleigh Fractionation

Partial Melting vs. Fractional Crystallization

Compatible vs. *incompatible* element plots

Fig. 3. A plot of trace element concentrations in two suites of igneous rocks. One suite is derived by 10-40% partial melting of a homogeneous parent, while the other suite is derived by 40% partial melting of the same homogeneous parent followed by 0-50% fractional crystallization (F = 1 to 0.5 respectively). Since D for trace element Ce is 0 in both suites, Ce follows a 1/F relation for both partial melting and differentiation. D for trace element R is 4 in both suites. Ce = 25 ppm and R = 100 ppm for a melt derived by 40% melting of the homogeneous parent.



(after Hanson, 1978. EPSL, 38, 26-43)

Other models are used to analyze

- AFC (Assimilation Fractional Crystallization) Tests
- ✓ AFC processes produce curved trends in both the trace element and isotopic concentrations
- However, AFC processes are difficult to recognize and require a strong contrast in trace element concentations between magma and wallrock before they can be detected (Powell, 1984)

Other models are used to analyze

Mixing of magmas

Tests (mixing equations): mixing produces

✓ linear trends in el-el plots

✓ hyperbolic trends
 in ratio-ratio/el plots
 ¹⁴³Nd/¹⁴⁴/Nd vs. ⁸⁷Sr/⁸⁶Sr
 ⁸⁷Sr/⁸⁶Sr vs. 1/Sr



Figure 7 ⁸⁷Sr/⁸⁶Sr vs. ²⁰⁶Pb/²⁰⁴Pb variations of Plio-Quaternary Italian mafic rocks. Central Italy orogenic magmatism falls along a mantle-crust mixing trend involving HIMU-FOZO and Upper Crust. Sicily, Sicily Channel, Sardinia and some Tyrrhenian Sea seamounts (anorogenic magmatism) plot along a mantle-mantle mixing trend involving at least two end members (HIMU-EM1).





 Le REE hanno proprietà chimiche e fisiche molto simili. Nondimeno, a causa della Δri (*contrazione dei lantanidi*) hanno la capacità di frazionarsi selettivamente nei processi di PM e FC.

Contrasts and similarities in the D values:

Also Note:

HREE are less incompatible especially in garnet

Eu can \rightarrow 2+ which conc. in plagioclase Table 9-1.Partition Coefficients for some commonly usedtrace elements in basaltic and andesitic rocks

		Olivine	Орх	Срх	Garnet	Plag	Amph
Rb		0.006	0.02	0.04	0.001	0.1	0.3
Sr		0.01	0.01	0.14	0.001	1.8	0.57
Ва		0.006	0.12	0.07	0.002	0.23	0.31
Ni		14	5	2.6	0.4	0.01	3
Cr		2.1	10	8.4	0.17	10	1.6
La		0.007	0.02	0.08	0.05	0.14	0.27
Ce	nts	0.009	0.02	0.34	0.05	0.14	0.34
Nd	me	0.009	0.05	0.6	0.07	0.08	0.19
Sm	Шe	0.009	0.05	0.9	0.06	0.08	0.91
Eu	th	0.008	0.05	0.9	0.9	0.1/1.5*	1.01
Tb	Ear	0.01	0.05	1	5.6	0.03	1.4
Er	Le l	0.013	0.31	1	18	0.08	0.48
Yb	Ra	0.014	0.34	0.2	30	0.07	0.97
Lu		0.016	0.11	0.82	35	80.0	0.89
data	fror	n Henderson	(1982)	* Eu ³⁺ /Eu ²⁺		Italics are es	timated

REE Diagrams

Plots of concentration as the ordinate (y-axis) against increasing atomic number

 Degree of compatibility increases from left to right across the diagram

La Ce Nd Sm Eu Tb Er Dy Yb Lu

Concentration



- Eliminate "saw-tooth" Oddo-Harkins effect and make yscale more functional by normalizing to a standard (see Rollinson,1993, pp142-148)
 - estimates of primordial mantle REE (ca. 2xchondrites)
 chondrite meteorite concentrations (Recommended values in Boynton, 1984)

• Garnet concentrates the HREE and fractionates among them. Thus if garnet is in equilibrium with the partial melt (a residual phase in the source left behind) expect a *steep negative slope in REE and HREE*

• Negative Europium anomaly develops when plagioclase is a fractionating phenocryst or a residual solid in source

2.22 Partition coefficients for REEs between minerals and basaltic melt. Garnet and plagioclase are the principal aluminous phases in basaltic magmas, but the former is stable at pressures above which plagioclase is stable. Note the striking contrast in their pattern of coefficients. Amphibole is another aluminous phase stable in hydrous systems. (Redrawn from Rollinson, 1993.)



(after Best, 2003)

Schematic chondrite-normalized REE patterns for basaltic rocks

Figure 2.3 Schematic chondrite-normalized REE patterns for basaltic rocks. Normalization constants from Nakamura (1974) are indicated on the diagram. (a) Strongly light-REE enriched basalt with very low concentrations of heavy REE suggests the presence of residual garnet in the source: extremely high concentrations of light REE suggest very small degrees of partial melting or a light-REE enriched source. (b) Basalt with a slight negative Eu anomaly which may have fractionally crystallized plagioclase or may have been in equilibrium with a plagioclase-bearing mantle source: heavy-REE concentrations of 10 \times chondritic suggest that garnet is absent from the source. (c) Basalt showing strong light-REE depletion, suggesting derivation from a light-REE depleted garnet-free source.



(after Wilson, 1989)

Spider Diagrams

An extension of the normalized REE technique to a broader spectrum of elements (multi-element diagrams)

 $\begin{array}{c|c} Chondrite-normalized\\ spider & diagrams & are\\ commonly & organized & by\\ increasing & incompatibility\\ Left \leftarrow Right \end{array}$

The order of the elements along the abscissa may vary slightly with different authors (Wood et al., 1979; Sun, 1980; Thompson, 1982, etc.)



Spider diagram for an alkaline basalt from Gough Island, southern Atlantic. After Sun and MacDonough (1989). In A. D. Saunders and M. J. Norry (eds.), Magmatism in the Ocean Basins. Geol. Soc. London Spec. Publ., **42**. pp. 313-345. (after Winter, 2001)

Spider diagram come indicatori petrogenetici

✓I pattern non vengono modificati in maniera significativa dai processi di FC e dal grado di PM e quindi riflettono le caratteristiche della sorgente (Pearce, 1983)

Conseguentemente, i magmi basaltici dei principali ambienti geottettonici (MORB, OIB, CFB, IAB) hanno pattern caratteristici

Spider Diagrams



FIGURE 3-8

A typical spider diagram pattern for mid-ocean ridge (MORB), ocean island (OIB), and island arc basalts. The ordinate scale is element abundance normalized to abundance in chonditic meteorites (see text). Normalization constants along the abscissa relate to estimates of abundances of each element in the primordial earth. [From M. Wilson, 1989, *Igneous Petrogenesis: A Global Tectonic Approach* (New York: Chapman & Hall), Fig. 2.4(a).]

Typical spider diagram for MORB, OIB and IAB normalized according to Thompson et al (1984). After Wilson (989).

MORB-normalized Spider

Separates LIL and HFS



Ocean island basalt plotted on a mid-ocean ridge basalt (MORB) normalized spider diagram of the type used by Pearce (1983). Data from Sun and **McDonough** (1989). From Winter (2001)

Trace elements as a tool to determine paleotectonic environment

- Useful for rocks in mobile belts that are no longer recognizably in their original setting
- Can trace elements be discriminators of igneous environment?
- Approach is empirical on modern occurrences
- Concentrate on elements that are immobile during low/medium grade metamorphism



(a) after Pearce and Cann (1973), Earth Planet, Sci. Lett., **19**, 290-300. (b) after Pearce (1982) in Thorpe (ed.), Andesites: Orogenic andesites and related rocks. Wiley. Chichester. pp. 525-548, Coish et al. (1986), Amer. J. Sci., **286**, 1-28. (c) after Mullen (1983), Earth Planet. Sci. Lett., **62**, 53-62 (after Winter, 2001).

✓ Isotopi come indicatori petrogenetici

L'uso degli isotopi come indicatori petrogenetici si basa su due assunti:

1. I rapporti isotopici in un magma rispecchiano quelli della sorgente (EBM process)*

* Non vale nel caso di *fusione in disequilibrio*:la Xisotopica del fuso è f delle fasi che fondono

2. Tali rapporti non vengono modificati dai processi di frazionamento**

** Vale per elementi con massa atomica >40 (Sr, Nd, Pb, etc). Elementi più leggeri (H, C, O,N, S) si frazionano (v. Appendix)

The Rb-Sr System: Review of Sr isotopes

• ⁸⁷Rb \rightarrow ⁸⁷Sr (decay constant $\lambda = 1.42 \times 10^{-11} \text{ a}$)

- Rb (parent) conc. in enriched reservoir (incompatible)
- Enriched reservoir

develops more ⁸⁷Sr over time

 Depleted reservoir
 (less Rb) develops less ⁸⁷Sr over time



After Wilson (1989). Igneous Petrogenesis. Unwin Hyman/Kluwer, in Winter 2001)

The Sm-Nd System

• Both Sm and Nd are LREE

- Nd > incompatible than Sm
- Sm/Nd ratio lower in partial melts than source

	Cs	Ba	La	Hf	Та	W	Re	Os	lr	Pt	Au	Hg	ТІ	Pb	Bi	Po	At	Rn
	132.91		138.91	178.49	180.95	183.84	186.21	190.23	192.22	195.08	196.97	200.59	204.38	207.2	208.98	(209)	(210)	(222)
7	87	88	89	104	105	106	107	108	109	110	111	112						30
	Fr	Ra	Ac	Rf	Db	Sq	Bh	Hs	Mt	Uun	Uuu	Uub						
	10001		(227)															

Lanthanide Series

18	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
40.12	140.91	144.24	(144.9)	150.36	151.97	157.25	158.93	162.5	164.93	167.26	168.93	173.04	174.97
2	04	03	00	04	O.C.	00	07	00	00	100	4/34	100	100

Review of Nd isotopes

REE diagram

Nd Sm

- ${}^{147}\text{Sm} \rightarrow {}^{143}\text{Nd}$ (decay constant $\lambda = 6.54 \text{ x } 10^{-12} \text{ a}$)
- Nd (daughter) enriched reservoir > Sm
- Enriched reservoir

 develops less ¹⁴³Nd over time
 Depleted res.
 (higher Sm/Nd) develops higher ¹⁴³Nd/¹⁴⁴Nd
 over time



After Wilson (1989). Igneous Petrogenesis. Unwin Hyman/Kluwer, in Winter 2001)

Isotope Correlation Diagram: Mixing between two sources



(after Peccerillo, 2007)

Appendix

Review of trace elements Chemical Fractionation and Distribution Coefficient (D)

Exchange equilibrium of a component *i* between two phases (solid and liquid)

 $i_{\text{(liquid)}} = i_{\text{(solid)}}$ $K = a^{i \text{ solid}}/a^{i \text{ liquid}} = \gamma X^{i \text{ solid}}/\gamma^{i} X^{\text{ liquid}}$ K = equilibrium constantFor dilute solutions can substitute D for K_D:

 $D = C_S / C_L$

Table 9-6 A brief summary of some particularly useful trace elements in igneous petrology

Element	Use as a petrogenetic indicator
Ni, Co, Cr	Highly compatible elements. Ni (and Co) are concentrated in olivine, and Cr in spinel and clinopyroxene. High concentrations indicate a mantle source.
V , Ті	Both show strong fractionation into Fe-Ti oxides (ilmenite or titanomagnetite). If they behave differently, Ti probably fractionates into an accessory phase, such as sphene or rutile.
Zr, Hf	Very incompatible elements that do not substitute into major silicate phases (although they may replace Ti in sphene or rutile).
Ba, Rb	Incompatible element that substitutes for K in K-feldspar, micas, or hornblende. Rb substitutes less readily in hornblende than K-spar and micas, such that the K/Ba ratio may distinguish these phases.
Sr	Substitutes for Ca in plagioclase (but not in pyroxene), and, to a lesser extent, for K in K-feldspar. Behaves as a compatible element at low pressure where plagioclase forms early, but as an incompatible at higher pressure where plagioclase is no longer stable.
REE	Garnet accommodates the HREE more than the LREE, and orthopyroxene and hornblende do so to a lesser degree. Sphene and plagioclase accommodates more LREE.
Y	Commonly incompatible (like HREE). Strongly partitioned into garnet and amphibole. Sphene and apatite also concentrate Y, so the presence of these as accessories could have a significant effect.
	Table 9-6. After Green (1980). Tectonophys., 63 , 367-385. From Winter (2001)

Stable Isotopes

- Stable: last ~ forever
- Chemical fractionation is impossible
- Mass fractionation is the only type possible

Example: Oxygen Isotopes

¹⁶ O	99.756% of r	natural oxygen
¹⁷ O	0.039%	66
¹⁸ O	0.205%	66

Concentrations expressed by reference to a standard International standard for O isotopes = standard mean ocean water (SMOW) ¹⁸O and ¹⁶O are the commonly used isotopes and their ratio is expressed as d:

 $d({}^{18}O/{}^{16}O) = \frac{({}^{18}O/{}^{16}O)_{sample} - ({}^{18}O/{}^{16}O)_{SMOW}}{({}^{18}O/{}^{16}O)_{SMOW}} x 1000$ result expressed in per mille (‰)

δ¹⁸O vs. ⁸⁷Sr/⁸⁶Sr



Figure 7.10 (a) Plot showing a positive correlation between δ¹⁸O and SiO₂ for a fractional crystallization-related calc-alkaline gabbro-diorite-tronalite-trondhjemite suite from an oceanic-arc plutonic complex in the Solomon Islands. (b) The same suite of rocks shows no correlation between ⁸⁷Sr/⁸⁶Sr and SiO₂. (Data from Chivas *et al.*, 1982.)

(after Rollinson, 1993)