种区分，额外的信息，例如，稳定同位素研究和放射性成因同位素-微量元素投影作图是十分必要的

2) 大陆地壳混染作用和 AFC 过程

DePaolo(1980)的研究表明，同化作用和分离结晶作用(Assimilation and Fractional Crystallization)(AFC)是一种常见的混染作用机制，可以使同位素相关图解远远偏离简单混合作用所显示的图形。在 Nd-Sr 同位素相关图解上，简单的混合作用确定了岩浆和混染物之间的直线趋势；而在 AFC 过程中，当 Nd 和 Sr 的总固体/液体分配系数显著不同时，那么样品投影点的变化趋势将明显偏离了简单的混合曲线。Powell (1984)改写了 DePaolo(1981b)提出的方程，并试图从同位素相关图解上计算混染物的组成。

3) 与海水的混染作用

海水相对地幔(如大洋地壳所见到的，图 6.13)而言具有所有的 $^{87}Sr/^{86}Sr$ 比值，这意味着在洋中脊体系中，海水和大洋地壳之间的 Sr 的交换，可能造成年轻的 MORB 及其相关的硫化物中具有相对较高的放射性成因 $^{87}Sr/^{86}Sr$(Spooner 等，1977；Vidal 和 Clauer，1981)。Nd 同位素则对这类混染作用相对来说不太敏感，在 Nd-Sr 同位素相关图解上，往往出现 $^{143}Nd/^{144}Nd$ 保持恒定不变，而 $^{87}Sr/^{86}Sr$ 则有明显增大的现象。变化矢量的长度与水/岩质量比值呈正比 Pb 同位素较难预测。Vidal 和 Clauer (1981)在研究东太平洋隆起时发现锶同位素呈现海水混染作用的证据，而 Pb 同位素则不同。然而，Spooner 和 Gale 对较大的白垩纪洋中脊硫化物矿床进行的类似研究中，却发现了海水 Pb 混染作用的证据。Chivas 等(1982)利用 Sr 同位素计算了经历海水蚀变作用的闪长岩和花岗闪长岩的水/岩比值，他们利用了和 Taylor(1974)使用过的氧同位素相似的方程(方程[7.14])。

3. 同位素对微量(和主要)元素投影

由于同位素比值不会因晶体-熔体平衡而发生分馏，因此可能反映岩浆源区的特征，同位素比值和一个主要元素或微量元素之间的相关图解可以用于作为指示源区的该主要元素或微量元素的标志。典型的图解是高度不相容微量元素(见第四章第七节和表 6.8)的比值，其在指示源区的化学成分方面最为有用。所以，同位素比值和高度不相容元素比值之间的相关图解可以用来说明成分不同的源区之间的混合作用。

Languir 等(1978)给出的方程预测，在一个同位素比值对具有共同分母的微量元素投影图解(例如，$^{87}Sr/^{86}Sr–1/^{86}Sr$)将给出一条直线。然而，这类混合作用图解可能会给出一个虚假的相关关系，因为其共同分母的效应的缘故(Dodson，1982；参见第二章第五节的讨论)，Mensing 等(1984)明确指出了 $^{87}Sr/^{86}Sr$ 比值对 1/Sr 图解存在的额外问题，是玄武质熔体经历了分离结晶作用并同化地壳物质(AFC)，混染物质的成分不落在岩浆演化轨迹上。因此，线性混合趋势不能用于确定混染物质的成分。

六、地幔-地壳地球动力学

确定地壳和地幔同位素储库的最终结果必然是一个可以解释储库如何相互作用以及它们如何获得其目前成分的岩石学模型。现代同位素地质学的主要成就之一就是建立了这样的统一模型，并能把储库组成与控制板块构造过程联系起来。仔细看来，有两种方法可以进行这方面的研究。基于 Pb 同位素的模型，主要展示地壳储库的特征，对人们认识大陆地壳的演化

起着重要作用。这种模型化过程被称为铅大地构造学(plumbotectonics)(或者叫做地幔柱大地构造学)。对于建立于若干种不同的同位素体系的研究基础之上，着重讨论地幔中的混合作用过程的模型，又可描述为“地球动力学模型”。

1. **地幔柱大地构造学(Plumbotectonics)(铅大地构造学)**

Doe 和 Zartman (1979)根据 Pb 同位素的判别能力而创立的模式说明了与大地构造背景相关的几个初始铅同位素组成的变化特征。他们指出由 U，Th 和 Pb 浓度可以确立三种储库(上部大陆地壳、下部大陆地壳和上地幔)(见表 6.6)。U，Th 和 Pb 集中于上部地壳，并且 U 和 Th 相对 Pb 而言更为富集，因此上部地壳的演化以富含放射性成因的铅为特征。下部地壳亏损 Th 和 U，以非放射性成因铅的演化为特点。地幔则含有比大陆地壳更低的 U，Th 和 Pb 浓度，但是其 U/Pb 和 Th/Pb 的演化必然也介于两者之间。Pb 在其三种储库的混合作用发生在“造山带”，从而产生了第四种“混合的”储库。

在他们的几种版本的模型中，Doe 和 Zartman (1979)以及 Zartman 和 Haines(1988)绘制了四种储库的 Pb 同位素随着时间的演化曲线。$^{207}Pb/^{204}Pb$ 对 $^{206}Pb/^{204}Pb$ 图解可以很好地判别出上部地壳和下部地壳/地幔，而 $^{208}Pb/^{204}Pb$ 对 $^{206}Pb/^{204}Pb$ 则较好地区分上部地壳和下部地壳/地幔(图 6.26)。

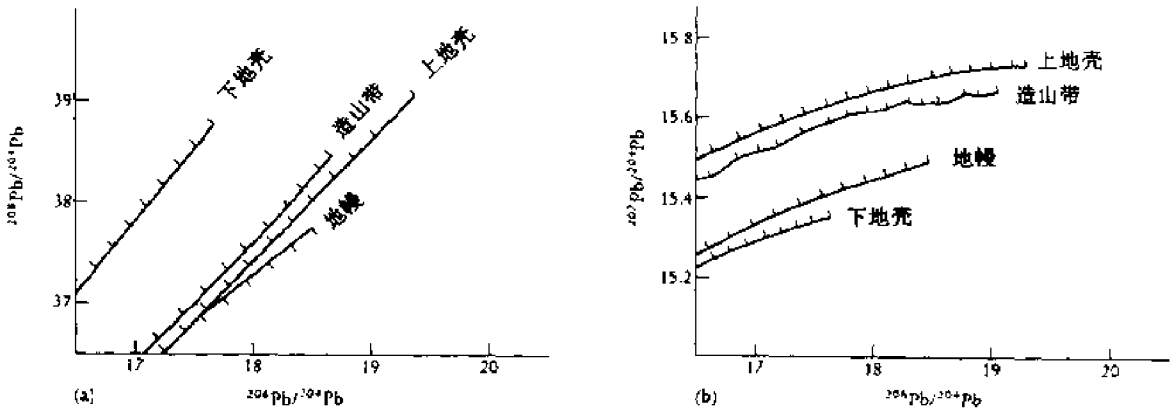


图 6.26 下部地壳、上部地壳、地幔和造山带的铅同位素演化曲线。(a) $^{208}Pb/^{204}Pb$ 对 $^{206}Pb/^{204}Pb$；(b) $^{207}Pb/^{204}Pb$ 对 $^{206}Pb/^{204}Pb$ (铅大地构造学)(取自 Zartman 和 Haines，1988)。每条曲线上的时间间隔为 100 Ma。

2. **地球动力学**

同位素示踪剂之间的相关关系必然导致人们寻找解释这些现象的原因，从而产生了一系列关于地球化学的大地构造模型。这些模型受到同位素资料及我们目前对大地构造过程的理解两个方面的制约。

例如，考虑一下从同位素相关图解所获取的早期观察成果之一，图 6.10 为大陆地壳和大洋玄武岩的 Nd-Sr 同位素相对于全地球成分的投影。相对于全地球而言，大洋玄武岩富集 Nd 而亏损 Sr，但大陆地壳却显示相反的关系。这说明大陆地壳和大洋玄武岩的地幔源区是 Nd 和 Sr 的互补储库，大陆地壳由地幔分异而来，使得残留下来的地幔储库富集 Nd 而亏损 Sr。

按同样的方式，地壳和地幔储库的同位素成分可以通过一系列地壳、地幔和全硅酸盐地球的初始成分之间的质量平衡而得到合理解释。假定涉及大陆地壳形成的地幔的比例和地幔对流作用的性质，我们就能够探讨不同储库之间的相互关系(Allegre 等 1983 a，b；Allegre，

1987；Galer 和 O'Nions，1985；Zindler 和 Hart，1986)。图 6.27 为说明不同源区间相互作用的可能方式的示意图。

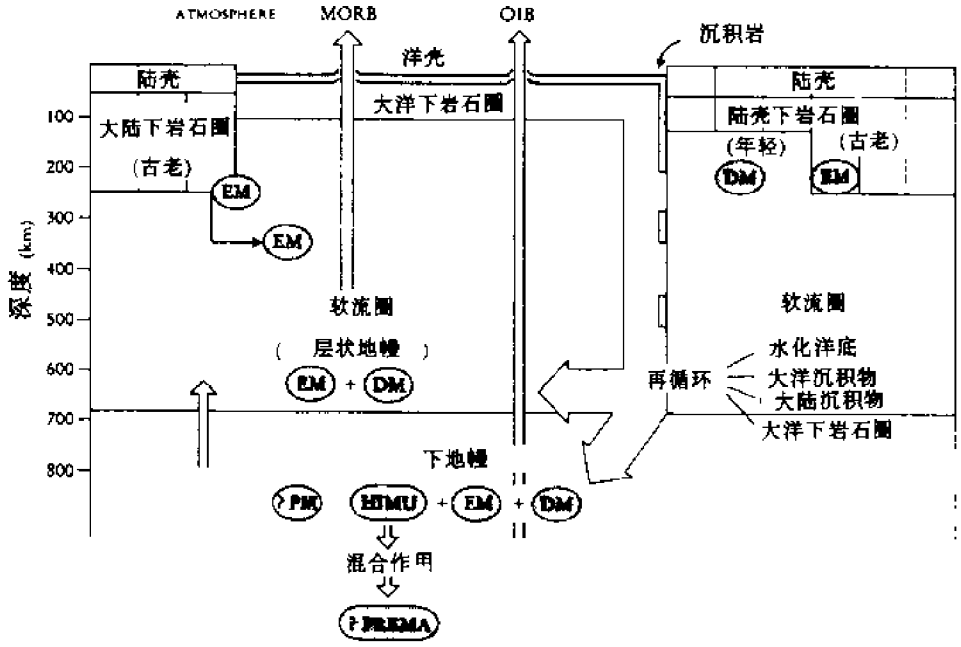


图 6.27 根据同位素地球化学的研究而建立的示意图，说明不同地壳和地幔储库以及它们之间可能的关系。Zindler 和 Hart(1986)定义的地幔储库：EM—富集地幔；DM—亏损地幔；HIMU-具有高 U/Pb 比值的地幔；PREMA—普通常见的地幔；PM—原始地幔。

第七章 岩石稳定同位素数据的运用方法

第一节 引　　言

大家知道，大多数天然元素都是由一个以上的稳定同位素所组成的。由于质量的差异，原子量小于40(即比Ca轻的)的元素其同位素之间可以通过物理过程而发生相互分馏，物理分馏的程度与质量差异的大小呈反比。原子量高于40的元素的同位素因相互间质量差异相对太小，以致不能发生同位素间的物理分离。

在地球化学中，稳定同位素是研究轻的元素如H，C，O，N和S的一个强有力的手段；利用其它方法难以对这些元素进行研究。这些元素通常是组成具有重要地质意义的流体的主要组分，因此可以用来直接研究流体以及水－岩相互作用效应的一个重要途径。另外，稳定同位素可以用来作为确定元素物质来源的示踪剂，也可以用作古温度计和研究地质过程中扩散和反应机制的手段。本章我们将介绍氢、氧、碳和硫等稳定同位素的用途，说明它们在阐明火成岩、变质岩和沉积岩的地球化学过程中的作用。更详细的解释可参阅 Hoefs (1987)和Valley等(1986)的著作。

习惯上，一般将稳定同位素转化为气体(如H_2，CO_2或SO_2)，然后在气体源质谱计上测定其同位素的组成。对于常见的O，H，C和S元素，样品的制备和分析过程中的污染问题必须十分小心，务必保证纯净的样品处理。然而，离子探针和激光显微探针越来越多地应用于稳定同位素分析，许多新近的研究已经展示了利用这些新技术能够分辨微细空间的同位素组成。

一、标记

稳定同位素比值的度量往往相对一个标准而进行，同位素比值表示为δ值，其单位是千分率(‰)。以氧同位素为例，其δ值按下式计算：

$$\delta^{18}O\ (‰) = \left[\frac{^{18}O/^{16}O_{(样品)} - ^{18}O/^{16}O_{(标准)}}{^{18}O/^{16}O_{(标准)}}\right] \times 1000 \qquad [7.1]$$

因此，若一样品的$\delta^{18}O$值为 +10.0，说明它相对标准样而言富集 ^{18}O 为 10‰；若另一个样品的$\delta^{18}O$值为 −10.0，则该样品相对标准样而言亏损 ^{18}O 为 −10.0‰。

二、同位素分馏

稳定同位素研究的主要目的就是要把它作为研究地质过程的一个手段，以同位素的质量

而非它们的化学成分为依据，讨论这些地质过程引起同位素之间的相互分馏。这种作用称为同位素分馏，在自然界存在三种方式的同位素分馏：

(1) 同位素交换反应。同位素分馏可以发生于同位素交换反应。例如，石英和磁铁矿之间氧同位素的交换：

$$2Si^{16}O_2 + Fe_3{}^{18}O_4 = 2Si^{18}O_2 + Fe_3{}^{16}O_4$$

同位素分馏作用受矿物的键强控制，遵从较轻的同位素形成较弱的化学键，而较重的同位素形成较强的键这样的一般规律。

(2) 动力学过程。动力学控制稳定同位素分馏作用反映一特定的同位素作好了反应的准备。当一个反应进行得不完全时，才能观察到动力学效应。

(3) 物理化学过程。如蒸发作用和浓缩作用、熔融作用、结晶作用和扩散作用等。

一个同位素在物质 A 和 B 之间的分馏可用分馏系数 α 来定义：

$$\alpha_{A-B} = \frac{\text{物质 A 中的同位素比值}}{\text{物质 B 中的同位素比值}} \qquad [7.2]$$

例如，^{18}O 和 ^{16}O 在磁铁矿和石英之间的交换反应，$^{18}O/^{16}O$ 在它们之间的分馏可表示为：

$$\alpha_{石英-磁铁矿} = \frac{\left(^{18}O/^{16}O\right)_{石英}}{\left(^{18}O/^{16}O\right)_{磁铁矿}}$$

其中$(^{18}O/^{16}O)_{石英}$和$(^{18}O/^{16}O)_{磁铁矿}$分别为实测的共生的石英和磁铁矿的氧同位素比值。如果同位素在被测的矿物中随机地分布在所有可能的原子位置上，那么α 和平衡常数 K 相关。

$$\alpha = K^{1/n} \qquad [7.3]$$

其中 n 是交换原子的数目。通常，把交换反应看成只有一个原子进行交换，即 $n = 1$，那么$\alpha = K$，即平衡常数与分馏系数相当。

分馏系数α的数值非常接近于 1，不同矿物间的分馏系数一般只在小数点后第三位上发生变化。所以，大多数α数值可写成 1.00X 的形式。例如，500°C 时 ^{18}O 在石英和磁铁矿之间的分馏系数为 1.009(Javoy，1977)。为了方便起见，α数值也可以表示为小数点后第三位数值的千分率，如石英磁铁矿的分馏系数为 9(或 9.0‰)。因此，分馏系数的一个有用的数学近似关系可写为：

$$1000\ln(1.00X) \sim X \qquad [7.4]$$

在上述讨论的情况中α=1.009，那么 $1000\ln\alpha \approx 9.0$。这个关系的重要意义在于，实验研究表明，$1000\ln\alpha$是矿物的矿物流体对的 $1/T^2$ 线性函数。这样便可以给出分馏系数的一般关系式：

$$1000\ln\alpha_{矿物1-矿物2} = A(10^6/T^2) + B \qquad [7.5]$$

其中 T 是绝对温度(°K)，A 和 B 是由实验确定的常数。对于石英-磁铁矿对，A 和 B 数值分别是 6.29 和 0(Chiba 等，1969)，其分馏系数关系为：

$$1000\ln\alpha_{石英-磁铁矿} = 6.29 \times 10^6/T^2$$

另一个有用的近似关系是 $1000\ln\alpha$和表示为δ数值的测量同位素组成。把两种矿物的δ数值之差表示为 Δ；当δ数值小于 10 时，Δ近似地等于 $1000\ln\alpha$。对于氧同位素在石英和磁铁矿之间的交换，存在：

$$\Delta_{石英-磁铁矿} = \delta_{石英} - \delta_{磁铁矿} = 1000\ln\alpha_{石英-磁铁矿} \qquad [7.6]$$

当δ数值大于 10 时，应使用表 7.1 中给出的关系式[7.12]。

三、物理化学对同位素分馏的控制

理解物理化学对稳定同位素分馏的制约，对于正确理解测定的稳定同位素比值是非常重要的，因为只有当分馏过程被完全理解了，才能正确地利用测量的δ数值来识别研究的元素的来源和所涉及到的地质过程。在这一小节里，我们简要地考察一下控制稳定同位素的物理化学条件因素。

温度是控制同位素分馏的重要因素之一。这一点从方程[7.5]可以很好地说明，同位素在平衡矿物对之间的分馏效应可以应用于同位素地质温度计(参见本章的第二、第四和第五节的有关内容)。

另一方面，同位素交换反应的相对体积变化非常小(氢同位素除外)。因此，压力效应对同位素分馏的影响事实上可以忽略不计。Clayton (1981)研究表明小于 20 kb 的压力对氧同位素分馏的效应低于 0.1%，落在分析测量误差之内。稳定同位素分馏缺乏明显的压力效应意味着可以在高压下研究同位素交换反应，其反应速率很快，将高压下的结果外推到低压范围，以讨论全域范围内压力的影响。

某些同位素分馏作用，尤其是生物体系，主要受控于动力学效应，例如，海水硫酸盐经细菌还原作用生成硫化物，轻的同位素 ^{32}S 比重的 ^{34}S 进行得要快 2.2%，其反应式可写成：

$$^{34}SO_4^{2-} \xrightarrow{k_2} H_2{}^{34}S \qquad [7.7]$$

$$^{32}SO_4^{2-} \xrightarrow{k_2} H_2{}^{32}S \qquad [7.8]$$

速率常数 K_1 比 K_2 大，它们的比值 $K_1/K_2=1.022$。封闭体系中的分馏效应可用 Rayleigh 分馏方程(第四章第二节)来模拟。

当同位素分馏发生于扩散作用过程中时，轻同位素相对于重同位素而言在输运方向上得到富集。扩散作用控制的同位素分馏在解释氧同位素作为温度计的结果时可能是非常重要的(参看本章的第二节)。在这个过程中，同位素被吸附到沉积物的粘土矿物中而发生分馏。较轻的氢、氧和硫同位素择优被吸附到粘土矿物上，导致建造水(formation water)中重同位素的富集(Ohmoto and Rye，1979)。

按照 Rayleigh 分馏定律，在蒸馏作用中，轻的同位素择优在蒸汽相富集。这个过程可以应用于天水的蒸发和浓缩过程，解释雨水和冰的$\delta^{18}O$ 和δD 的明显分馏作用。

一般来说，主要元素化学对稳定同位素的分馏影响非常小。然而，Taylor 和 Epstein(1962)的观察表明，硅酸盐矿物的氧同位素分馏可以根据矿物结构的平均键排列而解释，重同位素与高离子势的元素相联接。这一点可以石英和磁铁矿之间的 ^{18}O 分馏来说明，因为石英含半径小的和高电价的 Si^{4+}，因而富含 ^{18}O；而磁铁矿的 Fe^{2+}半径大，导致其含 ^{18}O 不足。斜长石的氧同位素组成是其 An 含量的函数。

重同位素富集在紧密堆积的晶体结构中。金刚石和石墨之间的碳同位素分馏作用早已为人们所熟知，方解石与文石之间的同位素差异则不大。α石英和β石英之间 ^{18}O 的变化也很小。

近几年来，研究表明方解石的氧和碳同位素的分馏作用受到结晶学控制。Dickson (1991)发现在单个方解石晶体中，不同结晶学形态的晶体表面具有不同的同位素组成。这表明同一晶体的不同晶面具有的键特征稍有差异，这足以导致氧和碳的同位素分馏。

第二节 氧同位素的运用方法

自然界存在三种稳定的氧同位素，它们的丰度如下：^{16}O=99.763%，^{17}O=0.0375% ^{18}O=0.1995%。

氧同位素研究中常用$^{18}O/^{16}O$比值，由方程[7.1]计算其δ数值。氧同位素测量中常用两种同位素标准。低温地质温度计测量(见本节的第二小节)相对于 PDB 而进行的(PDB-Carolina 南部白垩纪 Peedee 建造的箭石的同位素组成，也常作为碳同位素测量的标准)，而所有其它测量则相对标准平均大洋水(SMOW)而进行计算。SMOW 最初是假设的水样品，其氧和氢同位素比值与标准大洋水相似。当前的水样标准是由维也纳原子能机构提供的，被称为维也纳-SMOW 或者 V-SMOW。它的$^{18}O/^{16}O$比值与 SMOW 相同，D/H 比值在最初定义的 SMOW 的误差之内(Gonfiantini, 1978)。V-SMOW 的$\delta^{18}O$数值与 PDB 之间的关系由下式表示(Coplen 等, 1983)：

$$\delta^{18}O_{V\text{-}SMOW} = 1.03091\delta^{18}O_{PDB} + 30.01 \qquad [7.9]$$

$$\delta^{18}O_{PDB} = 0.97002\delta^{18}O_{V\text{-}SMOW} - 29.98 \qquad [7.10]$$

除 SMOW 外，有时也用 SLAP 标准(标准轻南极沉淀物)。它的$\delta^{18}O$数值为-55.5‰ SMOW(Gonfiantini, 1978)。

通过 F_2 或 BrF_5 与硅酸盐和氧化物反应把其中的氧释放出来，在高温下还原为 CO_2 以供质谱计测量。用纯的磷酸处理碳酸盐样品制备CO_2。当需测定水的氧同位素组成时，把水样与少量 CO_2 进行交换达到同位素平衡后，再测量 CO_2 的氧同位素组成。从已知的水-CO_2 分馏系数，便可把水的$^{18}O/^{16}O$比值计算出来。实验测定的$\delta^{18}O$数值的精度为 0.1‰~0.2‰的数量级内。

在本节中，我们首先考察自然界氧同位素的分布，然后考察氧同位素地质温度计的运用。随后讨论氧同位素与放射性成因同位素的相关图解，这种相关关系可以用于推测地质过程。

一、自然界$\delta^{18}O$的变化

自然界中$\delta^{18}O$值的变化达 100‰，其中一半发生在天水中(图 7.1)。球粒陨石具有非常有限的$\delta^{18}O$数值范围；地幔的$\delta^{18}O$值为 5.7 ± 0.3‰，这个数值似乎在地球和月球的整个历史中保持恒定(Taylor, 1980)。然而，Kyser 等(1980)发现 Hawaii 的碱性玄武岩比拉斑玄武岩富含$\delta^{18}O$达 0.5‰到 1.0‰，并根据测定的扩散速率(Graham 和 Harmon, 1983)提出它们来源于不同的地幔源区。因此，地幔的氧同位素组成存在小的不均一性。

大多数花岗岩、变质岩和沉积岩比地幔含有更高的$\delta^{18}O$值，而海水和天水亏损$\delta^{18}O$，因而构成互补的氧同位素储库。Deines(1989) 详细地评述了火成碳酸岩(carbonatite)的氧和碳同位素文献资料，其$\delta^{18}O$数值变化范围为+4‰至+27‰(SMOW)，但是原生未蚀变的碳酸岩为+6‰至+9‰。可见，原生碳酸岩的平均$\delta^{18}O$数值比地幔值稍微高一些；从玄武岩及其中的镁铁质和超镁铁质包体所获得的地幔的氧同位素组成范围是+5‰至+6‰。在 1000°C 时，地幔碳酸盐与硅酸盐之间的平衡$\delta^{18}O$分馏约为 2‰。因此，可以认为碳酸岩的氧来源于地幔。

二、氧同位素温度计

氧同位素研究在探讨地质问题中的第一个应用就是地质温度计。Urey(1947)提出钙的碳酸

盐相对海水而言富集 ^{18}O，与温度有关；这种关系可能用来确定古海水的温度。这一思想被迅速采纳，并用来计算了北半球的晚白垩纪海水的古温度。结果导致了根据矿物对之间 ^{18}O 的分配，建立了应用于较高温度体系的方法学。Clayton (1981)很好地评论了氧同位素温度计的方法和应用。

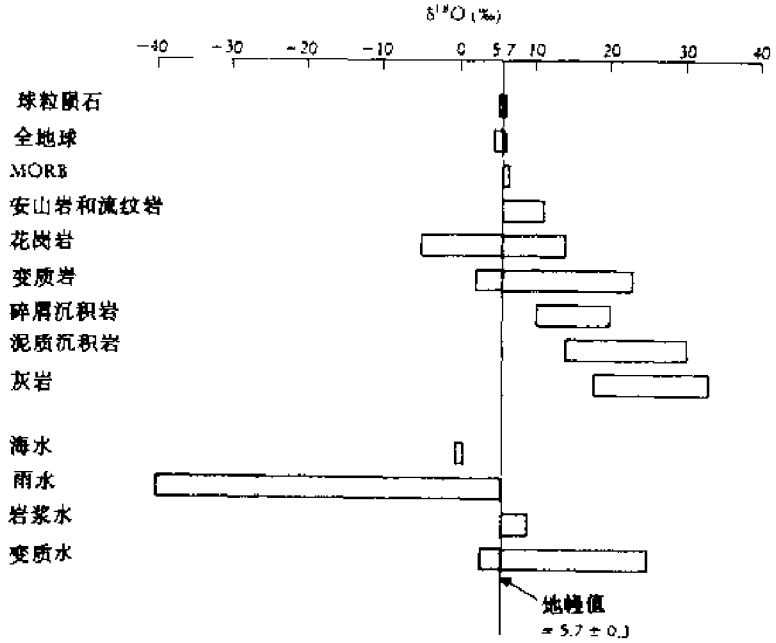


图 7.1 自然的氧同位素储库。数据引自：Taylor(1974)，Onuma 等(1972)，Sheppard(1977)，Graham 等(1983)和 Hoefs(1987)。

方程[7.5]给出了矿物对之间氧同位素交换与温度关系的总结性表达式。B 项经常是零，分馏系数简化为 $1/T^2$ 的函数。经验观察表明，在几百度的温度范围内 $\ln\alpha$ 与 $1/T^2$ 呈线性关系(图 7.2)，无水矿物(或相)对的这类投影应该通过原点。同位素分馏作用随着温度的增加而减小，因此氧同位素温度计可能在高温下不太灵敏。然而，同位素分馏效应的实验研究在高温下最为精确(见 Clayton 等，1989)，可靠的温度计已用来测定火成岩和变质岩的形成温度。氧同位素温度计比传统的阳离子交换温度计有许多优点，例如，可以测量同一岩石中许多矿物对的氧同位素交换。此外，像石榴石和辉石这样的氧扩散性低的矿物能够记录峰值温度条件。

1. 氧同位素温度计的校正

表 7.1 给出了许多不同的氧同位素交换反应的校准，其中有些给出了矛盾的结果。这显然引起了混乱，即这些校准能否作为可靠的地质温度计的基础。简而言之，有三种方法进行氧同位素交换温度计的校准：理论方法、实验方法和经验方法。

氧同位素分馏的理论计算是基于晶格动力学的研究，亦有根据晶体化学原理的计算方法，如增量法。这类研究结果和实验研究相吻合(Clayton 等，1989)，并可用来外推到实验结果之外的温度范围(Clayton and Kieffer，1991)。

根据矿物水同位素交换的研究业已用来校准氧同位素温度计，尽管现在已优先选用更可靠的矿物方解石交换反应(表 7.1)。

表 7.1 氧同位素温度计校准

按照 $1000\ln\alpha = A \times 10^6/T^2$，用实验确定的无水矿物之间的氧同位素分馏系数关系式中系数 A

(a)实验确定的矿物与方解石的平衡(Chiba 等，1989)

	Cc	Ab	An	Di	Fo	Mt
Q	0.38	0.94	1.99	2.75	3.67	6.29
Cc		0.56	1.61	2.37	3.29	5.91
Ab			1.05	1.81	2.73	5.35
An				0.76	1.68	4.30
Di					0.92	3.54
Fo						2.62

(b)实验确定的与水平衡(Matthews 等，1983)

	Ab	Jd	An	Di	Wo	Mt
Q	0.50	1.09	1.59	2.08	2.20	6.11
Ab		0.57	1.09	1.58	1.70	5.61
Jd			0.50	0.99	1.11	5.02
An				0.49	0.61	4.52
Di					0.12	4.03
Wo						3.91

(c)实验确定的(Bottinga 和 Javoy，1975； Javoy，1977)

	Ab	Pl	Px	Ol	Gt	Mt	Il
Q	0.97	1.59	2.75	3.91	2.88	5.57	5.29
Pl			1.08	2.32	1.29	3.98	3.70
P_x				1.24		0.21	

(d)用于计算矿物对间氧同位素分离作用的单个矿物多项式函数(Clayton，1991)[$X=10^6/T^2$，T 以 K 为单位]

方解石 $f_{Cc} = 11.781X - 0.420X^2 + 0.0158X^3$

石　英 $f_Q = 12.116X - 0.370X^2 + 0.0123X^3$

钠长石 $f_{Ab} = 11.134X - 0.326X^2 + 0.0104X^3$

钙长石 $f_{An} = 9.993X - 0.271X^2 + 0.0082X^3$

透辉石 $f_{Di} = 9.237X - 0.199X^2 + 0.0053X^3$

镁橄榄石 $f_{Fo} = 8.326X - 0.142X^2 + 0.0032X^3$

磁铁矿 $f_{Mt} = 5.674X - 0.038X^2 + 0.0003X^3$

*注：Ab-钠长石；An－钙长石；Cc－方解石；Di－透辉石，Fo－镁橄榄石；Il－钛铁矿；Jc－硬玉；Mt－磁铁矿；Ol－橄榄石；Pl－斜长石(An60)；Px－辉石；Q－石英；Wo－硅灰石。

方解石矿物氧同位素交换对相对高温而言是稳定的，其结果可以外推到实验条件范围之外。联立矿物方解石方程对便可给出矿物矿物对氧同位素分馏方程。最好的氧同位素温度计是矿物方解石对，它们在 $\ln\alpha$对 $1/T^2$ 图解上呈现最大的散度(图 7.2)。因此，石英透辉石是一个灵敏的矿物对，因为这两个矿物间氧同位素存在显著的分馏，而像石英钠长石这样的矿物对则不足以构成灵敏的温度计。石英磁铁矿分馏并未得到广泛地运用，因为氧在磁铁矿中的

高扩散性意味着它不能记录峰值温度。

氧同位素温度计经验校准是基于实验数据而进行的，然后应用于天然矿物组合(Botinga 和 Javoy，1973，1975； 参见表 7.1)。若岩石中所有矿物处于同位素平衡，那么这些地质温度计可以用来校准那些尚未进行实验的矿物对。然而，同位素平衡的这个假设很少能得到满足，使得这一方法的应用出现了不少问题(Clayton，1981)。

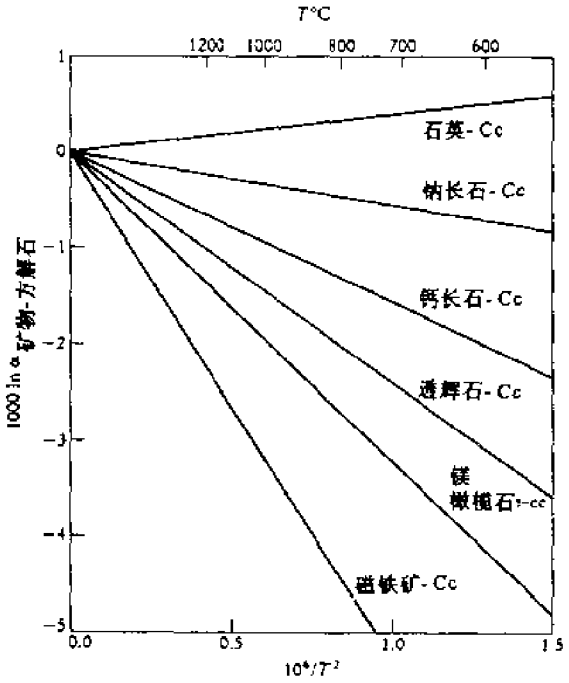


图 7.2 利用 Chiba 等(1989)的资料进行矿物-方解石对 1000lnα对 $10^6/T^2$ 的校正。

目前，最可靠的氧同位素温度计的校准方法是根据实验和理论研究的结果综合考虑的。Clayton (1991)综合了实验资料与理论研究成果，计算了许多普通造岩矿物的多项表达式(表 7.1)。这些表达式的联合便给出矿物对温度计。

2. 同位素平衡的识别

氧同位素地质温度计的优点之一就是在一种岩石中可能存在许多潜在的温度计，这种情形很少见于阳离子交换温度计。这就使得考察同位素平衡的假设是否成立成为可能。

Javoy 等(1970)提出利用一个等温投影作图的方法来判别同位素平衡。这个图解用氧同位素温度计方程(方程[7.5]与表 7.1)的参数 A 和[1000ln $\alpha_{石英-矿物}$ − B]项作为座标轴进行双变量投影作图。这样便可计算出研究体系的等温线，并且可以把矿物对的数据投影到图解上。如果一种岩石的矿物之间处于同位素平衡，那么它们的投影点则应该呈现平行于等温线的光滑变化趋势。Huebner 等(1986)利用这种图解说明麻粒岩相变泥质岩中矿物对之间同位素的不平衡(图 7.3)。

近来已经有人提出了，在缓慢冷却的岩石中同位素平衡应该是不可能的。Giletti (1986)的研究表明，在一种缓慢冷却的岩石中由于经过了矿物的冻结温度而停止了氧同位素交换，只有最后的矿物对交换氧同位素，才能达到平衡。Farver(1989)总结了扩散资料，表明在冷却的岩石中氧同位素封闭的次序是透辉石(最先封闭)、角闪石、磁铁矿、石英和钙长石(图 7.4)。

Giletti 的封闭温度方法构成了 Jenkin 等(1991)的估算同位素平衡的计算机模式。他们给出了一个 Fortran77 源程序。

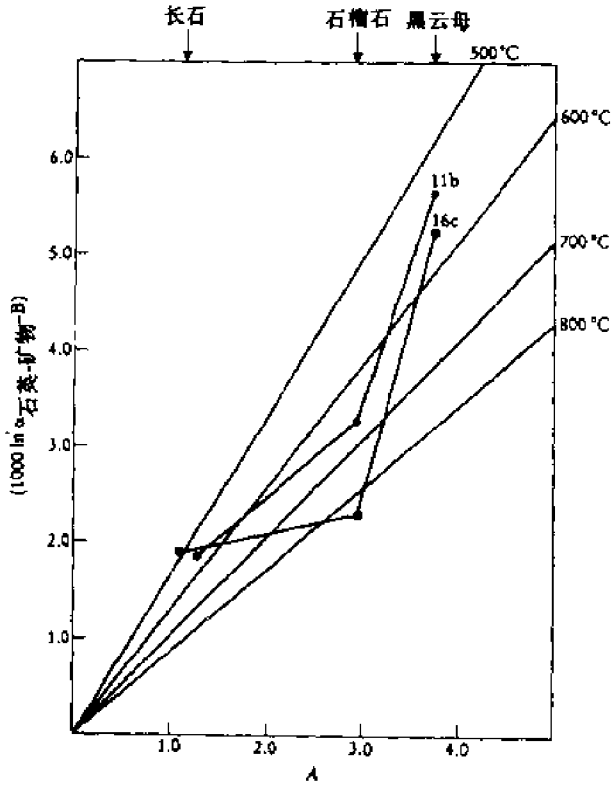


图 7.3 氧同位素等温线图解(Javoy 等，1970)，用来估计同一样品中矿物间同位素平衡的程度。依据氧同位素温度计方程[7.5]：$1000\ln\alpha_{矿物1-矿物2} = A(10^6/T^2) + B$，以$[A(10^6/T^2)]$和$[1000\ln\alpha_{石英-矿物} - B]$为变量分别作为 x 和 y 轴。等温线为 500°C 到 800°C，采用 Hueber 等(1986)的样品 11b 和 16c 的矿物对石英-长石、石英-石榴石和石英-黑云母的 $1000\ln\alpha$ 数据投影在图中，由 $\delta^{18}O$ 数值，按方程[7.6]计算 $1000\ln\alpha$ 数值。投影成分点说明石榴石的同位素组成不与黑云母和长石平衡。注意两个样品的长石成分略有不同。

然而，应该注意到岩石之中矿物对间平衡温度的差异只是同位素不平衡的一个原因，与外部流体发生同位素交换同样也能够解释同位素不平衡。这可以从两个共生矿物的δ数值的投影上得到评价。平衡相对 45° 斜率的直线来度量，这条直线代表矿物对的 $\Delta^{18}O$ 数值，是等温线，偏离 45° 线的任何趋势则表示同位素不平衡(图 7.5；Gregory 等，1989)。

3. 应用

氧同位素地质温度计测温方法可以应用于低温和高温两个方面。

1) 低温地质温度计

氧同位素在地质测温方面的最早应用是确定古海水的温度。这种方法假设海洋生物的碳酸盐外壳和海水之间的同位素达到了平衡，利用一直沿用的 Epstein 等(1975)方程进行古温度的估算，这个方程已被做了一些修正(Friedman 和 O'Neil，1977)：

$$T°C = 16.5 - 4.3\,(\delta_C - \delta_W) + 0.14(\delta_C - \delta_W)^2 \qquad [7.11]$$

其中 δ_C 和 δ_W 分别为海洋生物碳酸盐外壳和海水的 $\delta^{18}O$ 数值，可以通过测量 $CaCO_3$ 在 25°C 与 H_3PO_4 反应获得的 CO_2 的 $\delta^{18}O$，以及在 25°C 时与海水平衡的 CO_2 获得的 $\delta^{18}O$ 值。

这种方法假设过去海水的氧同位素成分与现在的相同，这一假设经常受到挑战，至少在更新的部分时间内这一假设必然夸大温度变化效应(Clayton，1981)。这个方法同样假设碳酸

盐的氧同位素组成是原始的，碳酸盐沉淀作用是平衡过程。值得注意的是，这两个假设都应该进行仔细检查。因为海洋底部海水的温度随着深度而作函数变化，也可以用氧同位素估计一些底栖海洋生物生活的海水深度。这即是所谓的氧同位素古深度计(Palaeobathymetry)。

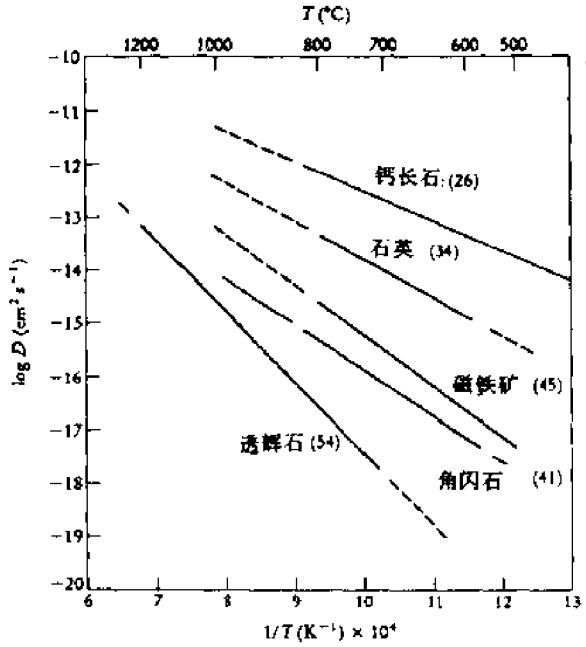


图 7.4 氧在矿物的 log 扩散系数对 $1/T^2$ 投影图解(Arrhenius 图解)　括号内的数字是活化能，单位是千卡/克原子氧(据 Farver，1989)。

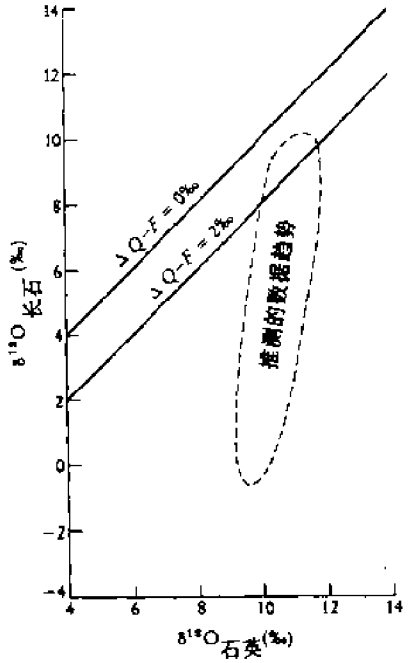


图 7.5　$\delta^{18}O_{石英}$对$\delta^{18}O_{长石}$图解，两条 45° 平行直线的$\Delta_{石英-长石}$分别为 0‰和 2‰。一个假设的不平衡趋势具有陡的正斜率。

低温同位素温度计也可用来确定成岩作用和低级变质作用温度，估计大陆地壳及洋底中活动地热体系的温度。

2) 高温地质温度计

高温下形成的岩石由于与结晶作用之后的流体发生再平衡作用，其原来的稳定同位素体系平衡特征经常遭到破坏。这个事实虽然可以用来推测有关水岩相互作用的性质(见本章第三节)，但是难以帮助确定火成岩和变质岩的固相线峰值温度。在水极少存在的体系中，如月球，氧同位素测温能够给出有意义的温度。Kyser 等(1981)已经获得地球熔岩和地幔包体的高温结果。在变质岩中，只有最低限度流体相互关系，Chiba 等(1989)和 Clayton 等(1989)新校准的温度计只对那些低扩散速率的矿物，如石榴石石英和辉石石英(见Connolly和Muchlenbachs，1988)作出有效承诺。下面给出利用变质泥质岩中石英辉石间氧同位素交换计算温度的实例。

(1)数据

麻粒岩相变质泥岩中共生的石英斜方辉石对(据 Huebner 等，1986 样品 Bb25C)：

$$\delta^{18}O_{\text{石英}} = 10.2‰，\ \delta^{18}O_{\text{斜方辉石}} = 7.9‰。$$

(2)理论

^{18}O 在石英和斜方辉石间的分馏与温度的关系由 Chiba 等(1989)和 Javoy (1977)给出的关系式为：$1000\ln\alpha_{Q\text{-}Opx} = 2.75 \times 10^6/T^2$

(3)计算

在这例子中，方程式[7.6]给出的近似已不合适，因为石英的值大于 10.0，所以我们利用下面公式计算：

$$\alpha_{A\text{-}B} = \frac{1000 + \delta_A}{1000 + \delta_B} \qquad [7.12]$$

这样，

$$\alpha_{Q\text{-}Opx} = 1010.2/1007.9 = 1.00228$$

$$1000\ln\alpha_{Q\text{-}Opx} = 2.279$$

由石英-斜方辉石氧同位素地质温度计：

$$2.279 = 2750000/T^2$$

$$T = 1098\ \text{K} = 825\ ^\circ\text{C}$$

三、氧同位素-放射性成因同位素相关图解

放射性成因同位素与氧同位素的相关图解具有非常重要的意义，因为这两种同位素的变化来自于完全不同的机制。这意味着这种相关图解所给出的信息量比单独的稳定同位素相关图解或者放射性成因同位素相关图解要丰富得多。

1. 地壳和地幔源区的识别

氧同位素提供了一种非常有效的手段，可以区分形成于与地幔平衡的岩石、以及那些形成于与大陆地壳平衡的岩石。在通常的情况下，大陆地壳比地幔富集$\delta^{18}O$(图 7.1)。这可能主要是由于大陆地壳和水圈之间长期相互作用的结果，在低温地质过程中 ^{18}O 分配到地壳矿物之中。因此，氧同位素是个有价值的指示地质过程的指示剂，是个说明岩石是否曾经与地球表面接触过的有效的示踪剂。

另一方面，放射性成因同位素说明地壳和地幔储库之间的同位素组成的差异，它们是母体/子体元素比值中长期性差异的函数，表明在漫长的地球历史中同位素储库相互间的孤立存在。这造成了地壳储库相对于地幔来说，其 $^{87}Sr/^{86}Sr$ 和放射性成因铅同位素的富集，而 $^{143}Nd/^{144}Nd$ 却亏损。

以下的讨论将集中在锶和氧同位素方面，但是所用的原理同样可以应用于其它放射性成因同位素-氧同位素对，常见岩石类型的氧和锶同位素成分范围如图 7.6 所示。

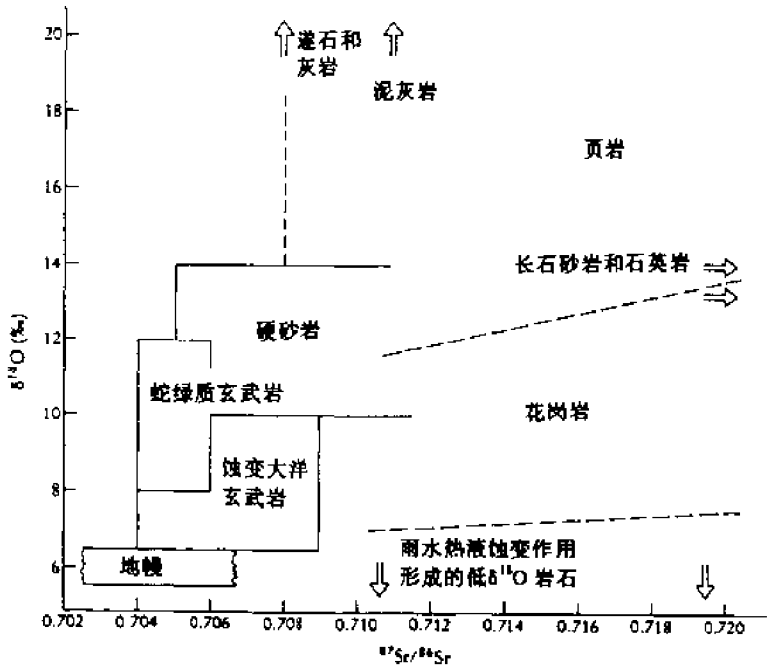


图 7.6 常见火成岩和沉积岩的$\delta^{18}O$ 和 $^{87}Sr/^{86}Sr$ 数值的变化范围(摘自 Magaritz 等，1978)

2. 地壳对火成岩混染作用的识别

相对地幔而言，地壳岩石富含放射性成因锶和氧同位素(图 7.6)，因此双变量 Sr-O 同位素相关图解是识别幔源岩石是否受到地壳混染的一个强有力的手段。研究表明，地壳混染作用存在两种机制：源区的混染作用和岩浆在上侵穿过大陆地壳过程中所遭受的混染作用。在 Sr-O 同位素投影图上(James，1981)，根据混合曲线的形态，便能区分这两类混染作用。当在源区混染物相对地幔而言富集 Sr，构成了整体相对较小的部分，那么混染作用在 $^{87}Sr/^{86}Sr$ 对$\delta^{18}O$ 混合曲线上以向下凸的形态为特征(图 7.7)。出现这种现象的原因是地壳物质不仅比地幔更富集 Sr，而其 $^{87}Sr/^{86}Sr$ 比值也比地幔的高，因此在两者混合物中占主导地位。然而，氧的浓度在所有岩石中大约相似。因此，派生熔体的氧同位素比值并没有极其显著地增大。$\delta^{18}O$ 的微小的增大是地壳物质对地幔物质的总比例的线性函数。Magaritz 等研究 Banda 弧的熔岩的资料呈现这种型式。

当熔体相对混染物而言富集 Sr，混染物的相对比例较高，那么在 Sr-O 同位素投影图的成分点则构成向上凸的曲线(James， 1981)。这可能是幔源熔体穿过大陆地壳受到混染的结果。此外，地壳混染作用使得主要元素和微量元素化学成分发生显著的变化，同时氧和放射性成因同位素比值呈现相关关系。

然而，地壳混染作用很少是个简单过程，经常涉及三种组分：熔体、正在沉淀的堆积相和混染物(Taylor，1980；James，1981)。这是大家熟悉的 Bowen(1928)首先提出的 AFC 过程。AFC 过程可以在放射性成因同位素-氧同位素相关图解上(图 7.9)，通过反曲式混合曲线得以识

别，这种混合曲线不会外推回源区或混染物的位置。Taylor (1980)给出了模拟的详细过程，Mauche 等(1989)给出了反曲式分布的实例。

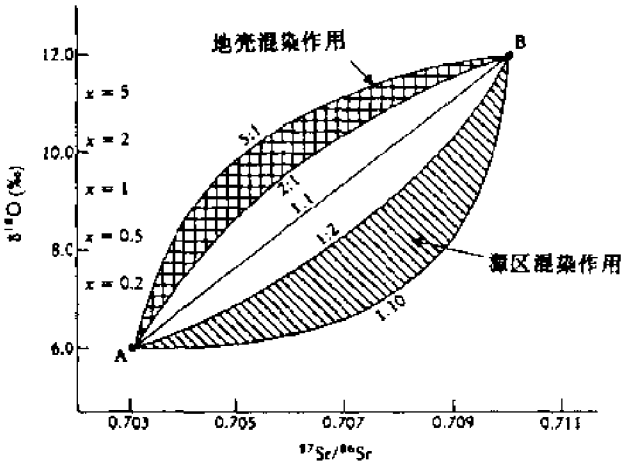


图 7.7 说明源区混合作用和地壳混染作用对地幔熔体的 Sr 和 O 同位素组成制约效应的假设混合作用图解(James，1981)。地幔源区(A)具有 $^{87}Sr/^{86}Sr$=0.703 和$\delta^{18}O$ = 6.0‰；地壳混染物(B)拥有 $^{87}Sr/^{86}Sr$ = 0.710 和$\delta^{18}O$ =12‰。曲线上数值是地幔中 Sr 与混染物中 Sr 的相对比值。在源区混染的情况下(斜线区)，(地幔 Sr)：(混染物 Sr)<1.0，引起向下凸的曲线形态，少量的混染物导致 $^{87}Sr/^{86}Sr$ 比值的重大变化。当出现地壳混染作用(方格区)的情况下，(熔体中 Sr)：(地壳中 Sr)比值可能大于 1.0，混合曲线呈现向上凸的特点。x 表示混染物(B)相对地幔(A)的比例。

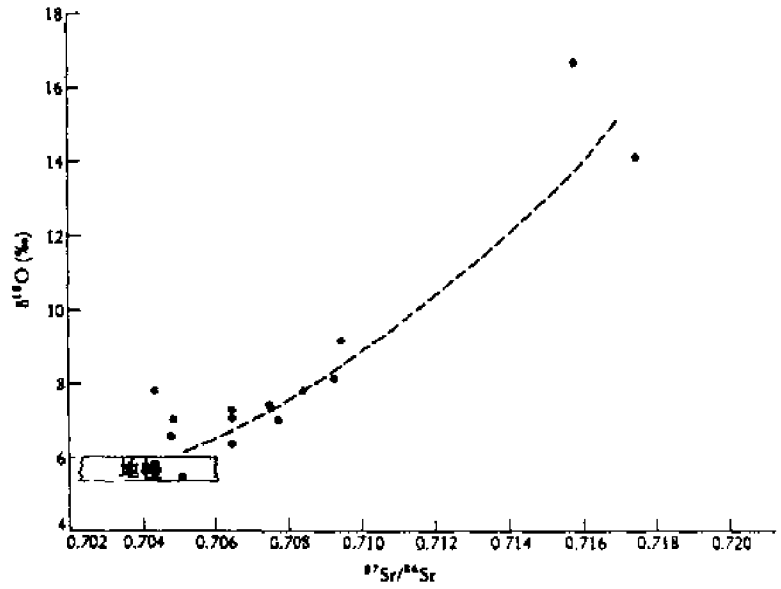


图 7.8 印度尼西亚 Banda 弧熔岩全岩样品的$\delta^{18}O$ 对 $^{87}Sr/^{86}Sr$ 图解。地幔的可能成分范围也表示出来。数据投影点构成的向下凸曲线(曲线的局部只有两个点来控制)，说明源区混染作用的存在(与图 7.7 相比较)。数据引自 Magaritz 等(1978)。

3. 火成岩的简单晶体分离作用的识别

一个没有遭受地壳混染的火成岩系统，一定反映其源区的放射性成因同位素特征，因为放射性成因同位素比值不受晶体-液体平衡(如晶体分离作用)所改变。另一方面，氧同位素的比值则随着晶体分离作用而出现小的变化，但是要求极端分离结晶作用方能产生小的$\delta^{18}O$ 变化。Chivas 在研究一个高度分异的大洋弧侵入岩套时说明了这一现象。在这些岩石中，氧同位素比值$\delta^{18}O$ 的变化从辉长岩的 5.4‰变化到细晶岩的 7.2‰。$\delta^{18}O$ 的增加与 SiO_2 的增加相

关；我们知道，SiO_2 是衡量岩浆分异作用的一个重要标志。然而，$^{87}Sr/^{86}Sr$ 则在测定的误差内保持恒定，不与 SiO_2 或者 $\delta^{18}O$ 相关(图 7.10)。

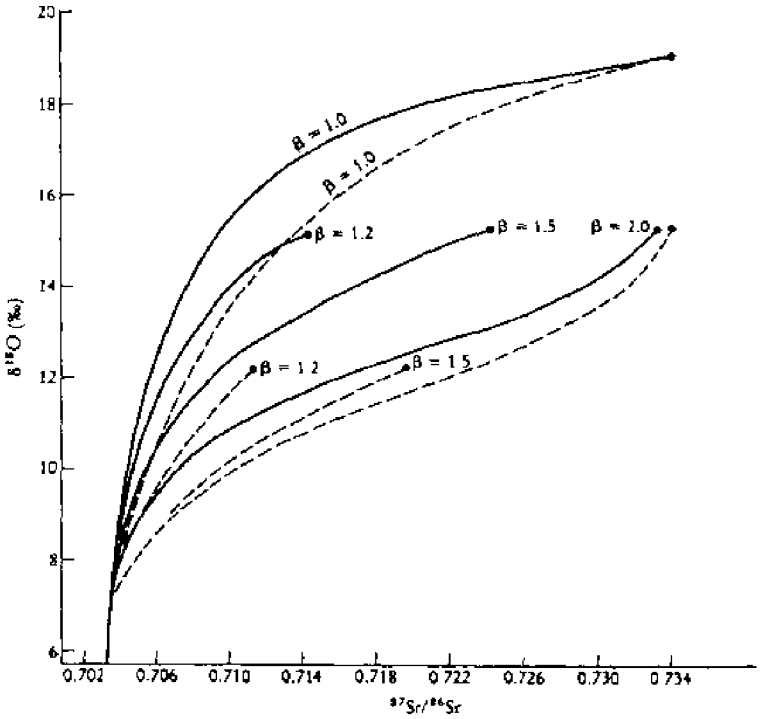


图 7.9 $^{87}Sr/^{86}Sr$ 对 $\delta^{18}O$ 的投影图，说明岩浆房中同化作用和分离结晶作用过程轨迹。熔体的初始成分是 $^{87}Sr/^{86}Sr = 0.703$，$\delta^{18}O = 5.7$。两套曲线代表两种不同的熔体 Sr 对混染围岩 Sr 的比值。实线代表熔体/围岩比值为 10:1，虚线代表的比值为 5:1。堆积物与被同化围岩的比值为 5:1。较高数值形成具有较低 $\delta^{18}O$ 数值。β 是 Sr 在堆积物中的含量对熔体中的含量的比值，即堆积物的 Sr 总分配系数。端点落在 99%的分离结晶作用(引自 Taylor，1980)。

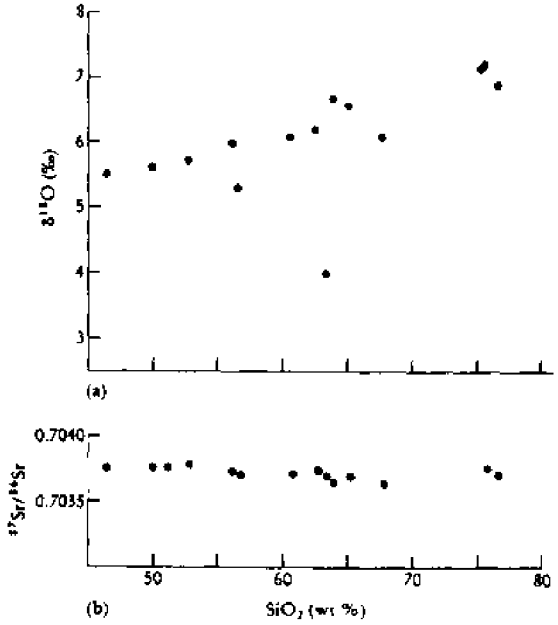


图 7.10 (a)Solomon 岛的一个大洋弧侵入杂岩体是由分离结晶作用形成的钙碱性辉长岩-英云闪长岩-更长花岗岩岩套，其 $\delta^{18}O$ 与 SiO_2 含量呈正相关；(b)而相同岩套岩石的 $^{87}Sr/^{86}Sr$ 比值和 SiO_2 不呈相关关系(资料引自 Chivas 等，1982)。

第三节 利用氧和氢同位素研究热水溶液：水岩相互作用

氧同位素和氢同位素研究的结合，是探讨涉及水溶液的地质过程的非常有力的武器。当制作δD 对$\delta^{18}O$的双变量投影图解时，可以发现不同的地质环境具有非常不同的同位素特征(图 7.11)。

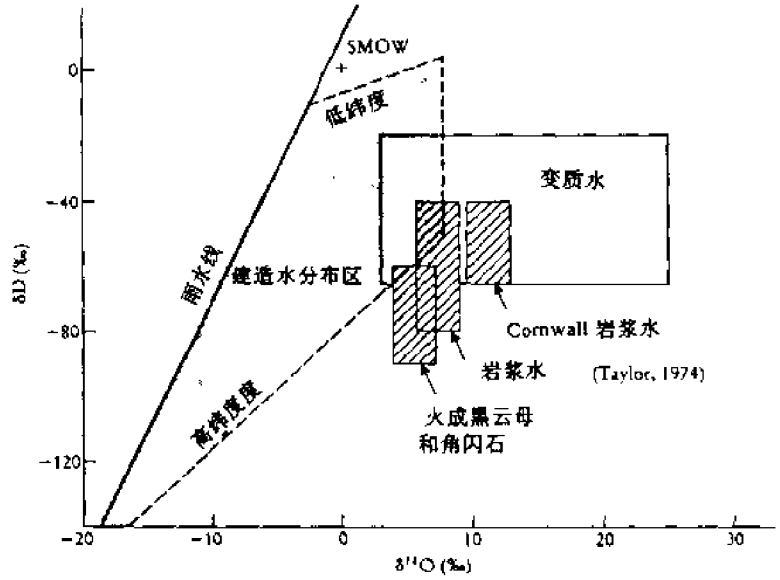


图 7.11 不同种类水的δD 对$\delta^{18}O$投影图。岩浆水和建造水的范围引自 Taylor (1974)。火成角闪石和黑云母引自 Taylor (1974)。Cornwall 花岗岩岩浆水引自 Sheppard (1977)。雨水线引用 Epstein 等(1965)和 Epstein(1970)。变质水的范围综合了 Taylor (1974)和 Sheppard(1981)的资料。

氢是大多数岩石的次要组分，因此除非当流体/岩石比值非常低，岩石和矿物的氢同位素对与之作用的流体的氢同位素成分非常敏感。然而，氧组成了常见岩石和矿物质量的 50%(在某些情况构成体积的 90%)，所以，岩石和矿物的氧同位素对与之作用的流体的氧同位素比值不大敏感，当然在非常高的流体/岩石比值条件下除外(见图 7.12)。

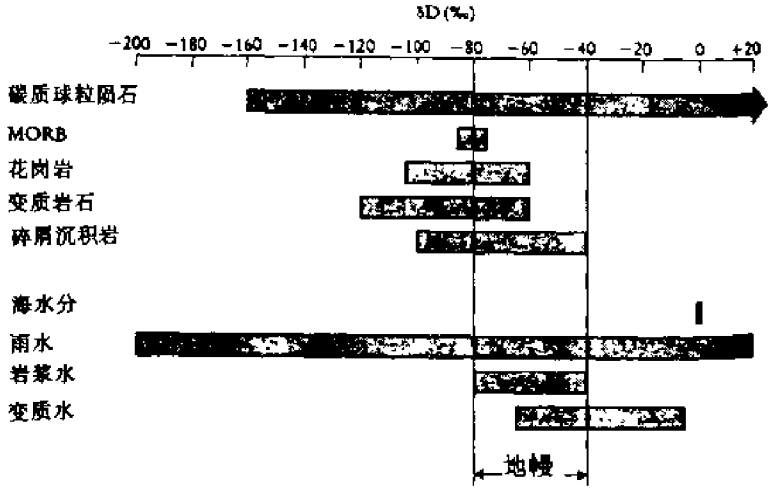


图 7.12 天然氢同位素储库。数据引自 Taylor (1974)；Graham 等(1981)，Kyser 等(1984)，Deloule 等(1991)以及 Hoefs(1987)

一、氢同位素

自然界存在两种氢同位素，它们的丰度是：$^{1}H = 99.9844\%$，$^{2}D = 0.0145\%$ (重氢，或氘)。氢的这两种稳定同位素之间的相对质量差异是最大的，其结果导致天然产出的矿物的氢同位素组成变化范围极大。此外，氢同位素在自然界以 H_2O，OH^-，H_2 和碳氢化合物形式而普遍存在。

氢同位素的测量以千分率为单位，用 SMOW 作为标准，计算方法与氧同位素相类似(参见方程[7.1])，表示为 δD‰，其测量精度为 1‰和 2‰之间；SLAP 的δD 数值相对 SMOW 是 −428‰。D/H 比值的测定一般是以气体 H_2 为对象，常用的办法是在高温下由还原反应将待测样品制备成气体 H_2，然后上质谱计测定其 D/H 比值。

常见岩石类型和水的δD 数值如图 7.12 的总结所示。地幔数值通常的范围为−40‰～−80‰，但是 Deloule 等(1991)给出的数值可低达−125‰。据认为 MORB 储库的δD=−80% ± 5%(Kyser and O'Neil，1984)。

二、由矿物同位素组成计算水的同位素组成

不同地质环境中的水的同位素组成，可以通过直接测量保存在液体包裹体的水而获得(Ohmoto 等，1974；Richardson 等，1988)。然而，最常见的做法是，通过间接地测量与水溶液平衡的矿物的同位素组成来确定水的同位素组成。

有一种近似的方法，若假设某种造岩矿物与一种热液之间的同位素达到了平衡，那么造岩矿物和水之间同位素平衡的实验室校准便可以用来计算水热液的同位素组成。氧和氢同位素的实验校准资料(表 7.2 和表 7.3)使得我们能够确定与矿物平衡的水的同位素组成。计算时要求知道平衡温度的数据，可以估计或者用液体包裹体测温等方法来确定平衡温度。这方法的研究实例可以参照 Hall 等(1974)的成果。他们讨论形成 Colorado Climax 钼矿床的热液水的来源。在此研究中，热液的温度由包体测温所获得，水的δD 和$\delta^{18}O$ 组成是利用实验校准的白云母水同位素平衡关系式由白云母和绢云母的同位素组成计算而来。以下举例说明 Colorado Climax 钼矿床与白云母平衡的水的同位素组成的计算步骤

数据：

$\delta^{18}O_{白云母} = +7.4‰$，$\delta D_{白云母} = -91‰$

温度 T=500℃ (由流体包裹体测温而来，资料引自 Hall 等 1974 的样品 C131-70)。

水的氧同位素组成的计算：

白云母的氧同位分馏方程(O'Neil and Taylor，1967)是：

$$1000\ln\alpha = -3.89 + 2.38\ (10^6/T^2)$$

当 $T = 500℃ = 773K$

所以 $1000\ln\alpha = 0.0931$

因为 $\Delta_{白云母-水} = 1000\ln\alpha$

所以 $\delta^{18}O_{白云母} - \delta^{18}O_{水} = 0.0931$

已知 $\delta^{18}O_{白云母} = +7.4‰$

故 $\delta^{18}O_{水} = +7.3‰$

水的氢同位素的计算：

白云母-水之间氢同位素分馏方程(Suzuoki 和 Epstein，1976)是：

$$1000\ln\alpha = 19.1 - 22.1(10^6/T^2)$$

在 T = = 500℃ = 773K 时，

$$1000\ln\alpha = -17.89$$

由于

$$\Delta_{白云母-水}=1000\ln\alpha$$

$$\delta D_{白云母}-\delta D_{水}=-17.89$$

$$\delta D_{水}=-73.1‰$$

由图 7.11 不难看出，与白云母平衡的水的氢氧同位素组成落在岩浆水区域内，说明形成矿床的热液为岩浆热液。

三、天然水的同位素组成

天然水的同位素组成可以用直接测量的方法或用上述介绍的计算方法来获得。Taylor(1974)介绍了六种天然水的同位素组成(图 7.11)。不同类型水的同位素特征可以用来示踪热液的来源。

1. 大气水(雨水)

大气水是所有天然水中同位素组成变化范围最大的水。δD 和$\delta^{18}O$ 的变化构成了一条线性关系直线，即所谓的雨水线，可以按下式来表示(Taylor，1979)：

$$\delta D‰=8\delta^{18}O+10 \qquad [7.13]$$

雨水的$\delta^{18}O$ 和δD 数值随着纬度而呈现规律性的变化。热带大洋岛的雨水δD 和$\delta^{18}O$ 的值接近于零，而大陆高纬度地区的$\delta^{18}O$ 可低达−20 ~ −25，δD 数值为−150 ~ −250。两者的极端变化及线性关系起因于大气水的浓缩作用。极端变化反映水因蒸发作用离开海洋，随着空气在向大陆的移动过程中其$\delta^{18}O$ 数值不断降低。雨水线为线性关系表明：同位素分馏作用是一个平衡过程，D/H 的分馏与 $^{18}O/^{16}O$ 呈正比。

2. 大洋水

现代海洋水的组成是非常均一的，其$\delta^{18}O$ = 0‰和δD = 0‰。唯有的例外是具有高蒸发速率的地区，如红海，那里的海水的$\delta^{18}O$ 和δD 数值都有所增大；或者那些受到淡水稀释的海洋水，其氧同位素组成由于与大洋地壳的物质交换而得到缓冲，这个观点强烈地受到了 Gregory 和 Taylor(1984)研究的支持。他们研究 Oman(图 7.16)的 Semail 蛇绿岩的氧同位素的分布，其结论说明了这一点。

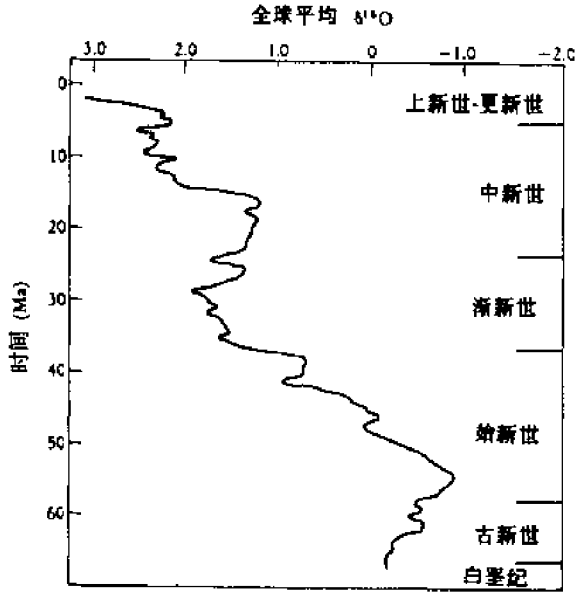


图 7.13 整个第三纪时期海水的$\delta^{18}O$ 组成的变化。这个记录是基于底栖有孔虫的氧同位素组成而获得的(据 Miller 和 Fairbanks，1985)。

表 7.2 根据方程 $1000\ln \alpha_{矿物-水} = A + B(10^6/T^2)$，矿物-水之间氧同位素分馏作用常数

矿物	实验温度范围 (°C)	A	B	文献资料
重晶石	100~350	-6.79	3.00	Friedman 等(1977)
方解石	0~700	-3.39	2.78	O'Neil 等(1969)
白云石	252~295	-3.24	3.06	Matthews 等(1979)
石　英	200~500	-3.40	3.38	Clayton 等(1972)
	500~750	-1.96	2.51	Clayton 等(1972)
	250~500	-3.31	3.34	Matsuhisa 等(1979)
	500~800	-1.14	2.05	Matsuhisa 等(1979)
碱性长石	350~800	-3.41	2.91	O'Neil and Taylor (1967)
	500~800	-3.70	3.13	Bottinga 等(1973)
钠长石	400~500	-2.51	2.39	Matsuhisa 等(1979)
	500~800	-1.16	1.59	Matsuhisa 等(1979)
钙长石	350~800	-3.82	2.15	O'Neil 等(1967)
	400~500	-2.81	1.49	Matsuhisa 等(1979)
	500~800	-2.01	1.04	Matsuhisa 等(1979)
斜长石	350~800	(-3.41-0.14An)*	(2.91~0.76An)	O'Neil 等(1967)
	500~800	-3.7	3.13~1.04An	Bottinga 等(1973)
白云母	400~650	-3.89	2.39	O'Neil 等(1967)
	500~800	-3.10	1.90	Bottinga 等(1973)
金红石	575~775	1.46	4.10	Addy 等(1974)
磁铁矿	500~800	-3.70	-1.47	Bottinga 等(1973)
高岭石	不确切	2.87	2.5	Land 等(1978)
绿泥石	66~175	见以下公式		Savin 等(1988)
$[Mg_{2.5}Fe_{0.5}(OH)_6][Al_{1.5}Fe_{1.5}][AlSi_3O_{10}][OH_2]$: $-11.97 + 2.67X + 2.93X^2 - 0.415X^3 + 0.037X^4$　(其中 $X=10^3/T$)				

*注：An 是钙长石的摩尔分数。

海水在过去的同位素组成较少能够被完全肯定。海相碳酸盐氧同位素组成的证据表明，在第三纪期间海洋的同位素成分存在着全球性的变化(图 7.13)。这些变化据认为是由于极地区域的冰储存轻的氧同位素而引起的。人们已详细地了解这些变化特征，并利用同位素组成变化曲线作为地层学的工具。奥陶纪腕足贝壳的未蚀变部分的氧同位素组成也有类似的变化(Marshall 等，1990)，但是这种模型的不确定性之一，就是成岩变化对计算的古海水同位素组成有一定程度的影响。尤其对于那些上新世－更新世之前的沉积碳酸盐，

3. 地下热水

现代地下热水来自雨水，但是通过与围岩的同位素交换使之同位素组成向较高的$\delta^{18}O$ 值方向变化。δD 数值与原来的雨水相同或者略为富集(增大)。洋底的地热体系的$\delta^{18}O$ 数值介于+0.37 和+2.37 之间，接近于未受调整的海水(Campbell 等，1988)。

表 7.3 按照方程 $1000\ln \alpha_{矿物-水} = A+B(10^6/T^2)$，矿物－水之间氢同位素分馏作用常数*

矿物	实验温度范围(℃)	A	B	文献资料
白云母	450~800	19.1	22.1	Suzuoti 等(1976)
黑云母	450~800	-2.8	22.3	Suzuoti 等(1976)
角闪石	450~800	7.9	23.9	Suzuoti 等(1976)
	350~850*	23.1 ± 2.5	31.0	Graham 等(1984)
	850~950*	1.1		Graham 等(1984)
透闪石	350~650	21.7	31.0	Graham 等(1984)
	650~950	14.9		Graham 等(1984)
阳起石	400	29.0		Graham 等(1984)
钠铁闪石	不确定	52.0		Graham 等(1984)
高岭石/迪开石	100~250	0.972~0.985		Marumo 等(1980)
绢云母	100~250	0.973~0.977		Marumo 等(1980)
绿泥石	100~250	0.957~0.987		Marumo 等(1980)
黝帘石	280~650	27.73	15.7	Graham 等(1984)
绿帘石	<300	138.8	29.2	Graham 等(1984)
	300~650	-35.9 ± 2.5		Graham 等(1984)

*注：亚铁质非闪石质普通角闪石。所有矿物 $1000\ln \alpha_{矿物-水} = 28.2 - 22.4(10^6/T^2) + (2X_{Al} - 4X_{Mg} - 68X_{Fe})$，其中 X_A 是指 Al 在黑云母、白云母或角闪石中的摩尔分数。Suzuoki 等(1976)。

4. 建造水

沉积盆地的建造水呈现宽阔的$\delta^{18}O$ 和δD 的数值变化范围(图 7.11)。单个盆地的建造水的氢和氧同位素组成之间通常构成一线性关系，代表雨水和其它来源水(如捕获的海水)的混合，或天水与围岩间的同位素发生了交换作用。

5. 变质水

已经进行了许多尝试，来计算变质作用范围内与变质矿物平衡的水的$\delta^{18}O$ 和δD 数值(Taylor，1974；Rye 等，1976；Sheppard，1981)。这些数据的综合便可获得变质水方框，其$\delta^{18}O$ 为+3‰和+25‰之间，δD 为-20‰到-65‰之间(图 7.11)。

6. 岩浆水

计算岩浆水的同位素组成是相当困难的工作，因为许多岩浆与地下水发生了相互作用。然而，Taylor (1974)计算的原生岩浆水区域所确定的δD 值为-40‰~-80‰，$\delta^{18}O$ 值为+5.5‰~+9.0‰。Sheppard(1977)的研究表明，与产于地壳熔融的英国西南部的二叠纪花岗岩有关的岩浆水δD 值为-40‰~ -65‰，$\delta^{18}O$ 值为+9.5‰~ +13‰(图 7.11)。

四、水/岩比值的定量化

水-岩相互作用能够变化于两个极端之间。当水/岩比值小时，岩石的$\delta^{18}O$ 占体系的主导地位，流体成分变化与地热体系发生的那样。另一方面，当水/岩比值很大时，水的$\delta^{18}O$ 占体系的同位素组成的主导，那么岩石的$\delta^{18}O$ 数值就会被调整。从 Taylor(1974，1977)推导的质量平

衡方程及$\delta^{18}O$ 数值，便可计算水/岩比值。对一个封闭体系，如果没有水的丢失，水/岩比值(W/R)(在热液体系的活动寿命内所积累的水/岩石比值)是：

$$(W/R)_{封闭} = \frac{\delta^{18}O_{岩石}^{最终} - \delta^{18}O_{岩石}^{初始}}{\delta^{18}O_{流体}^{初始} - \delta^{18}O_{流体}^{最终}} \qquad [7.14]$$

这是有效的水/岩比值，它与取决于交换反应效率的实际水/岩比值不同。岩石的氧同位素初始比值($\delta^{18}O_{岩石}^{初始}$)可以从具体岩石类型的“通常”数值而获得，或者岩套中未蚀度岩石样品的分析值。最终岩石(蚀变岩)的($\delta^{18}O_{岩石}^{最终}$)数值为测量值。流体开始的($\delta^{18}O_{流体}^{初始}$)数值为假设的(如现代海水)或对于雨水的情况，由蚀变矿物组合的 D/H 比值和雨水方程计算而得到。流体的最终同位素组成($\delta^{18}O_{流体}^{初始}$)可从蚀变岩石的矿物计算而来。有时候把斜长石(An30)的$\delta^{18}O$ 值近似地看作为岩石的$\delta^{18}O$ 值，这是因为在大多数岩石中长石的含量较高，它表现为与外来液体交换 ^{18}O 的速率最大。如果能够独立地估计水/岩相互作用的温度，那么我们就可以用长石水分馏方程来计算水的同位素组成(见表 7.4)。

如果水/岩相互作用发生在一个开放体系，那么水/岩比值方程可以由 Taylor(1977)给出的公式进行估算，这里假定水只作单一方向通过该体系：

$$(W/R)_{开放} = [\ln (W/R_{封闭}) + 1] \qquad [7.15]$$

任何给定的热流体系介于两个极端情况之间都是可能的。下例根据 Talylor (1974，1977)方程计算水/岩比值，并以图 7.14 来说明。

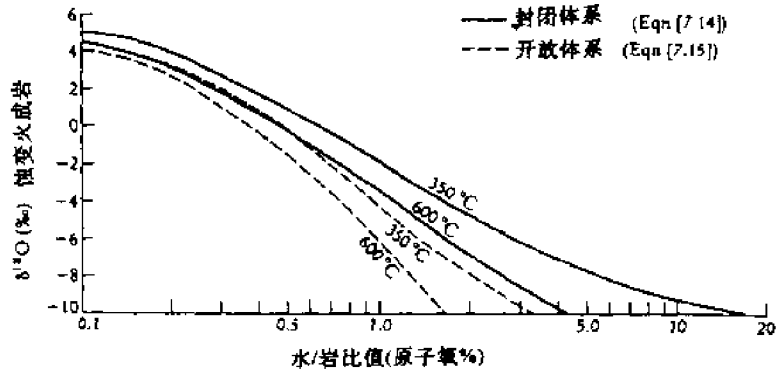


图 7.14 根据开放体系水/岩比值[7.15]方程和封闭体系水/岩比值方程[7.14]计算的热液蚀变岩石的$\delta^{18}O$值投影图。模型假设岩石初始$\delta^{18}O$值为+6.5，水的初始$\delta^{18}O$值为−14；计算了 500°C 和 600°C 的变化曲线；实线为封闭体系[方程 7.14]，虚线为开放体系[方程 7.15](方程 7.14 和 7.15 据 Taylor，1974)。

(1) 数据：初始岩石同位素组成：$\delta^{18}O = 6.5‰$，

最终岩石同位素组成：$\delta^{18}O = -4.0‰$

初始流体同位素组成：$\delta^{18}O = -14.0‰$。

(2)最终流体同位素组成的计算：

按表 7.4 给出的斜长石(An30)-水方程：

$$1000\ln \alpha_{斜长石-水} = (-3.41-0.14An) + (2.91-0.76An)(10^6/T^2)$$

$$= -3.46 + 2.682\,(10^6/T^2)$$

当 $T = 500°C = 773°K$ 时，

$$\Delta_{斜长石-水} = 0.97$$

假设$\delta^{18}O_{斜长石} = \delta^{18}O_{全岩}$(最终的氧同素组成)

$$\delta^{18}O_{水} = -4.0-0.97 = -4.97$$

最终水的氧同位素组成：$\delta^{18}O = -4.97‰$

(3)水/岩比值的计算：

A.由封闭体系水/岩比值方程[7.14]，知：

$$(W/R)_{封闭} = \frac{\delta^{18}O_{岩石}^{最终} - \delta^{18}O_{岩石}^{初始}}{\delta^{18}O_{流体}^{初始} - \delta^{18}O_{流体}^{最终}}$$

$$= \frac{-4-6.5}{-14-(-4.97)} = 1.16$$

B.通过开放体系方程[7.15]，得到：

$$W/R_{开放} = \ln(W/R_{封闭}+1) = 0.77$$

图 7.15 表示不同水/岩比值对花岗闪长岩的δD 和$\delta^{18}O$ 同位素组成的影响。利用黑云母的同位素组成监测δD 的变化，用长石的同位素组成监测$\delta^{18}O$ 的变化(Taylor，1977)。在小的水/岩比值(达到 0.1 岩石体积)情况下，花岗闪长岩的氧同位素组成实际上不变化，而δD 值则减小大约 100%。随着水/岩比值的增大，$\delta^{18}O$ 值迅速减小，而δD 却保持恒定。

五、水-岩相互作用的实例

Taylor 及其同事对水-岩相互作用的深入研究成果在地球化学的许多领域具有广泛的应用

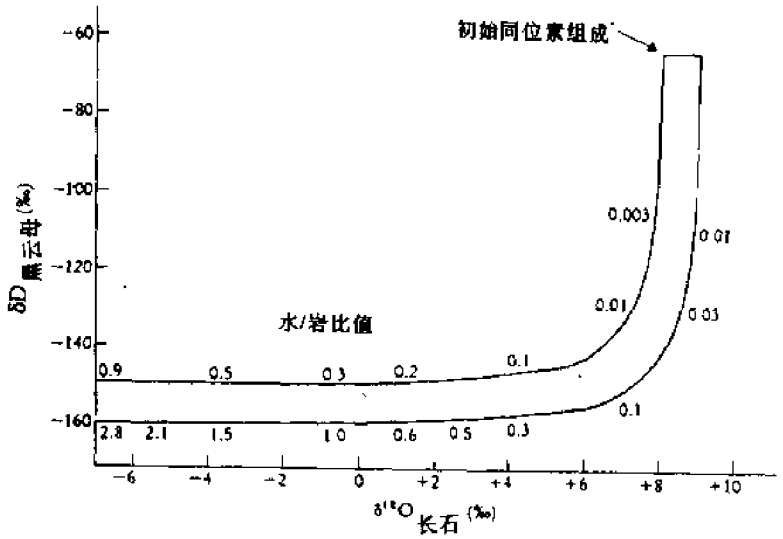


图 7.15 δD 对$\delta^{18}O$ 图解，说明花岗闪长岩与地下水发生了同位素交换；其中黑云母的 D 和长石的 ^{18}O 的变化情况。投影曲线说明δD 和$\delta^{18}O$ 随着水/岩比值的变化而变化的范围。初始长石的组成$\delta^{18}O$ 为+8.0 到+9.0，黑云母δD 为-65.0，地下水的δD 和$\delta^{18}O$ 分别为-120 和-16。黑云母和水之间在 400°C-450°C 时 D 的分馏为$\Delta_{黑云母-水} = -30$ 和 -40；长石和水在 400°C-450°C 时$\delta^{18}O$ 的分馏为$\Delta_{长石-水} = 2.0$。小的水/岩比值对黑云母的δD 和长石$\delta^{18}O$。上面的曲线表示水/岩比以重量为单位，下面的曲线以体积为单位(引自 Taylor，1977)。

性。以通常的术语而言，氧同位素对热液流体的灵敏性意味着它是检测新鲜岩石中热液蚀变作用的良好手段，譬如 Rautenschlein 等(1985)的研究例子。更具体的，水的来源和性质可以被认识，它相对围岩的体积可以得到定量化的研究。下面就简要地评述一些研究实例。

1. 火成侵入体与地下水间的相互作用

Taylor 及其同僚的许多开创性研究工作说明高位火成侵入体周围经常伴随着热液循环体系(参见 Taylor，1977，1978 的评述性论文)。他们发现这些侵入岩的围岩相对于“正常”值，其δD 和$\delta^{18}O$ 发生显著亏损，侵入岩及围岩中的矿物对岩浆成因数值来说在同位素上是不平衡的。他们的结论是：这种同位素效应是由于和雨水相互作用的结果，并提出侵入岩体起着一个热机作用，促使围岩中的地下水构成一个热液对流体系。水/岩比值的变化范围从<<1.0 变到大约 7.0。

这些研究成果为建立火成岩的初始同位素组成的尝试提供了重要依据，因为首先必须清除那些同位素明显受到干扰的岩石。同样，应该引起重视的是，对于采自高位地壳的侵入岩样品的同位素温度计的解释必须要谨慎从事。另外，一些火成岩已完全与地下水再平衡的事实亦为放射性成因同位素研究提出了警示。

2. 洋底玄武岩与海水间的相互作用

大量研究表明，海底玄武岩现已保存在蛇绿岩之中，明显地经历了与热液流体的同位素交换，这种流体最大可能是海水。

例如，Stakes 和 O'Neil(1982)已计算了东太平洋隆起年轻玄武岩与海水相互作用的水/岩比值超过 50。热液循环体系汲取冷的海水，运移到附近活动的岩浆房被加热。这样产生的热的海水据认为是形成蛇绿岩中的块状硫化物矿床的热液来源。这一假说业已被在洋中脊喷向海底的高温热泉这一令人振奋的发现所证实，正是这种高温热泉形成了富含硫化物的矿床(本章第五节)。

Schiffman 等(1987)研究了塞浦路斯 Troodos 蛇绿岩——蚀变玄武岩，说明它们在温度为 310°C 和 375°C 之间已和$\delta^{18}O$ 接近零值的海水发生了反应。与未蚀变玄武岩相比，其微量元素含量也有所改变，计算表明流体/岩石比值介于 10 和 20 之间。

Gregory 和 Taylor(1981)详细研究了阿曼 Semail 蛇绿岩，表明相对于平均大洋地壳而言，其上层富集$\delta^{18}O$，而下部辉长岩亏损$\delta^{18}O$(图 7.16)。这种数值特征是由于氧同位素在硅酸盐

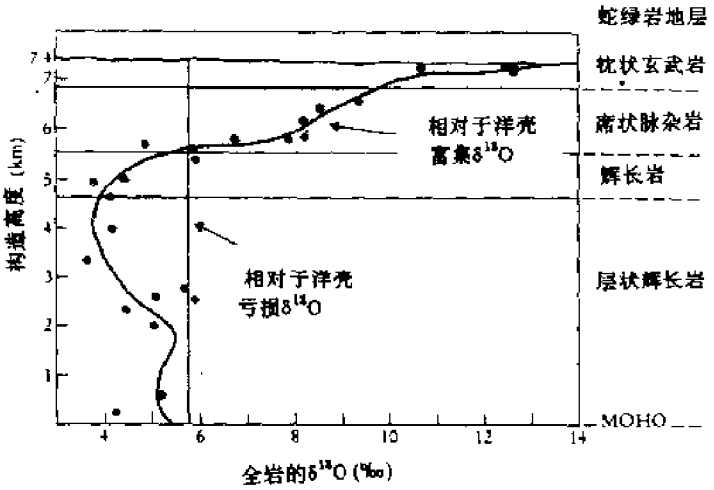


图 7.16 阿曼 Semail 蛇绿岩剖面的全岩$\delta^{18}O$ 数值随构造标高(km)而变化的情况，反映了$\delta^{18}O$ 的相对富集和亏损是蛇纹岩地层学的函数。实圆点表明测量点。按 Gregory 和 Taylor(1981)的资料修正。

矿物和水之间的分配取决于温度的原因。Gregory 和 Taylor(1981)同样亦作了重要观察，表明

Semail 蛇绿岩数据反映$\delta^{18}O$ 在海水和大洋地壳之间的净交换是零。这意味着海水的$\delta^{18}O$ 组成受到大洋底的成分所缓冲。这一观察结果被 Campbell 等(1988)的测量所证实。

3. 变质岩中的水-岩相互作用

稳定同位素研究可以用来确定变质岩中水/岩相互作用的两个不同特征。一方面，氧同位素研究能够确定流体运动的型式，而氢和氧同位素的联合可以用来确定最初与变质岩平衡的流体的同位素组成。

水的存在与否对变质岩中同位素平衡具有重要的控制作用，使得矿物对之间及岩石类型之间的稳定同位素平衡更容易达到。例如，流体的存在与否可以解释不同作者的研究结果出现明显偏差的原因；若没有流体存在，经受了一定变质级别的互层沉积岩在变质过程中没有达到同位素平衡(参见 Bolltrell 等，1990；Valley 和 O'Neil)。然而，若有流体存在，在其它变质地体中这种变质岩却呈现氧同位素组成的高度均一，说明同位素达到了平衡(Chamberlain 等，1988；Rumble 等，1983；Wiekham and Taylor，1985)。这种差异可进一步通过考察不同的水/岩比值效应和变质地体中流体流动型式来进行解释。

变质岩中的水/岩比值变化非常之大，从外部导源水的巨大通量(Wickham 和 Taylor，1985)变化到麻粒岩相岩石中的非常小的数值(水/岩比值介于 0.1 和 0.0) (Valley 和 O'Neil，1984)。作为一般的情况，水/岩比值可能随着递进变质作用过程中的脱水反应而不断减小。流体可能是渗透性的，其流动不受构造控制，水通过裂隙离开岩石(Valley 和 O'Neil，1984)。

Chamberlain 等(1985)，Rumble 等(1983)以及 Wickham 和 Taylor(1985)根据氧同位素的研究推测了流体流动图。

然而，光靠氧同位素研究还不能确定富氧流体的精确性质，因为 H_2O，CO_2 和硅酸盐熔体都是富氧储库。因此，还需要氢同位素研究的配合以便了解具体流体的来源。Wickham 等(1985)利用这个方法研究了法国 Pyrenees 泥质岩中白云母的同位素组成，表明存在大量海水的涌入，并与围岩发生了氧同位素交换，达到了同位素均一化，并且测量的同位素组成大约在 450 °C 时接近于盆地建造水。

4. 热液矿床形成过程中的水-岩相互作用

美国矿床学杂志 Economic Geology (1974，No.6)用了相当的篇幅专门讨论了热液矿床形成过程中水的来源问题，其中 Taylor(1974)作了一篇精彩的评论性文章。正如所预料的那样，热液矿床的形成过程中水的类型千变万化。例如，斑岩铜矿可能形成于岩浆水和被加热的雨水间的相互作用，而塞浦路斯型块状硫化物矿床的形成则可能与海水相关。密西西比河谷型 Pb-Zn 矿床的形成与加热的建造水有关，其盐度和同位素组成与油田卤水相一致。Kerrich 等(1979)在研究加拿大太古代 Abitibi 绿岩中的金成矿作用时，根据与石英平衡的水的高$\delta^{18}O$ 值得出结论，认为水在成因上是变质水，成矿流体来源于递进变质作用过程中的脱水作用。

5. 碎屑沉积物的成岩作用

成岩矿物与沉积孔隙水之间的 ^{18}O 分馏作用可以用来计算水的同位素组成，或者矿物生长温度，如果已知水的同位素组成。Ayalon 等(1988)说明了如何利用 Alberta 上白垩统砂岩中成岩矿物顺序排列的同位素组成，研究砂岩自埋藏到抬升过程的流体演化和热历史。他们引用了矿物-水方程(如绿泥石、伊利石、蒙脱石、方解石、高岭石和石英，参见表 7.4)。Girard 等(1989)进行了相似的研究，他们利用流体包裹体测温资料，结合 K/Ar 年龄的确定和孔隙流体的$\delta^{18}O$ 数值的计算，来估计下白垩统长石砂岩的时间、温度、埋藏历史。

第四节 碳同位素的应用

在自然界，碳有 ^{12}C 和 ^{13}C 两个稳定同位素；它们的丰度是：$^{12}C = 98.89\%$，$^{13}C = 1.11\%$ 。碳同位素的测量标准是 Carolina 南部白垩纪 Peedee 建造中的拟箭石，以 PDB 表示。选择这一标准的原因是它的 ^{13}C 和 ^{18}O 丰度和平均海相石灰岩相接近。PDB 标准样已经用尽了，目前的标样是碳酸岩标准样(NBS-18)和海相石灰岩标样(NBS-19)。碳同位素组成的标记方法与氧相似：

$$\delta^{13}C = \left[\frac{\left(^{13}C/^{12}C\right)_{样品} - \left(^{13}C/^{12}C\right)_{标样}}{\left(^{13}C/^{12}C\right)_{标样}}\right] \times 1000 \qquad [7.16]$$

碳同位素的测定方法是先将样品制备成 CO_2，再用气体源质谱计测定其 $^{13}C/^{12}C$ 比值，按[7.16]标记成$\delta^{13}C‰$，其精度一般好于 0.1‰。碳酸盐经纯磷酸的处理或者热分解制成 CO_2。有机化合物一般用高温氧化方法(氧化的火焰)或用 CuO 氧化剂进行样品的前处理。

一、碳同位素在自然界的分布

碳在自然界既可以其氧化态形式存在(CO_2、碳酸盐和复碳酸盐)，也可以还原态的碳(如甲烷和有机碳)形式存在，或呈金刚石和石墨。图 7.17 总结了天然物质的碳同位素组成范围。陨

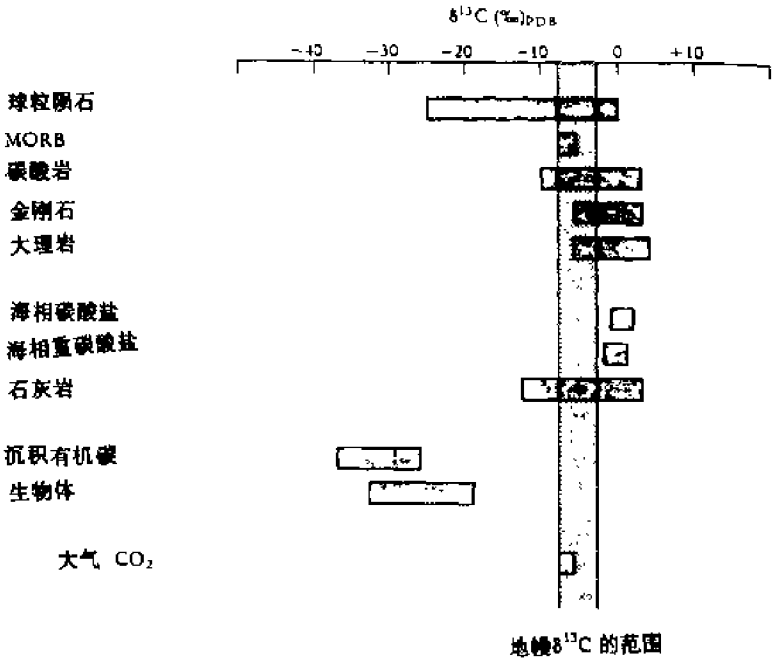


图 7.17 自然界的$\delta^{13}C$ 储库。天然含碳样品的$\delta^{13}C$ 范围，数据取自 Kerridge (1985)，Exley 等(1986)，Field 等(1986)，Hoefs(1987)和 Schidlowski(1987)。

石具有变化范围较宽的碳同位素组成。例如，碳质球粒陨石的总$\delta^{13}C$ 组成可变化为 -25‰到 0‰ (kerridge，1985)。碳酸岩、金伯岩和金刚石的同位素研究所确定的地幔数值的范围较窄，其$\delta^{13}C = -3‰ \sim -8‰$，通常以其平均值 -6‰代表地幔碳同位素组成。MORB 的平均$\delta^{13}C = -6.6‰$(Exley 等，1986)。按照定义，海水的$\delta^{13}C$ 值接近于 0‰；海相碳酸盐的$\delta^{13}C$ 值变化范围狭窄，介于 $-1‰ \sim +2‰$，而海相复碳酸盐介于 $-2‰ \sim +1‰$。然而，古海水都没有这种

恒定的碳同位素组成，下面还会以现代海水值来进一步进行讨论。

生物成因(有机)碳在同位素上以亏损 ^{13}C 为特征。无机碳通过 CO_2 固定机制进入生物中而择优富集轻的 ^{12}C 同位素。这个过程主要受控于反应动力学控制，其结果利于轻同位素的富集。这种分馏作用的净效应是相对幔源碳而言(其$\delta^{13}C$ 约为 $-6‰$)，存在两种互补的碳同位素储库。一方面，生物物质强烈亏损$\delta^{13}C$ ($-20‰$到$-30‰$；按 Schidlowsk 1987 的研究，地球上生物的平均值为($-26‰\pm7‰$))，而海水及海相碳酸盐富集$\delta^{13}C$(约为 0)。甲烷是所有有机碳化合物中 ^{13}C 最为亏损的，它一般形成于有机物质的厌氧发酵作用或者石油或干酪根在高于 100°C 时的热分解。生物成因的甲烷的$\delta^{13}C$ 值约为 $-80‰$。

1. 碳同位素分馏的控制因素

碳同位素分馏作用受平衡过程和动力学过程控制。平衡分馏过程如图 7.18 所示，在多数情况下$\delta^{13}C$ 的分馏与温度强烈有关。然而，应该注意到一个普通的平衡过程即溶解和再沉淀作用，并不引起碳同位素发生显著的分馏。

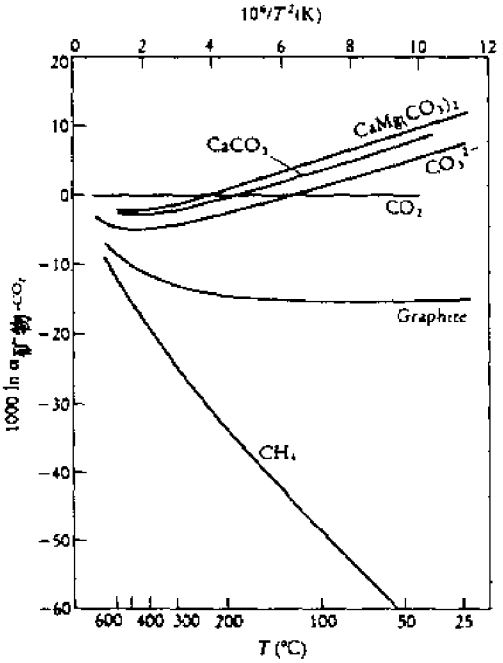


图 7.18 碳的种类对 CO_2 的分馏(据 Ohmoto 和 Rye，1979)

动力学分馏作用对生物体系十分重要。例如，CO_2 固定为有机碳的过程，在成岩过程中有机物经厌氧发酵作用而形成的甲烷，都会引起碳同位素发生分馏。在这些情况下，分馏作用受反应速率所控制，较轻的同位素更容易参与反应。当反应涉及到碳和氧的时候，动力学效应将会按相应的方式影响它们的同位素。因此，$\delta^{18}O$ 和$\delta^{13}C$ 之间存在相关关系是预料之中的事情。

二、碳酸盐的碳和氧同位素研究：$\delta^{18}O$ 对$\delta^{13}C$ 的投影

碳酸盐的氧和碳同位素的综合研究是区分不同成因碳酸盐的有效手段。图 7.19 表示地球和陨石碳酸盐的$\delta^{18}O$ 对$\delta^{13}C$ 图解。成分相对 PDB 标准进行投影，虽然目前已越来越多地利用

SMOW 作为碳酸盐的$\delta^{18}O$ 测量标准。运用方程[7.9]和[7.10]可以进行 PDB 和 SMOW 数值的相互转化，但是为明了起见有必要再重述一下，海相碳酸盐的$\delta^{18}O$ 值(PDB)是零；而海水的$\delta^{18}O$ 值(SMOW)也是零。

Epstein 等(1953)方程给出了两者的关系，如方程[7.12]所述两者平衡温度约为 16.9℃。

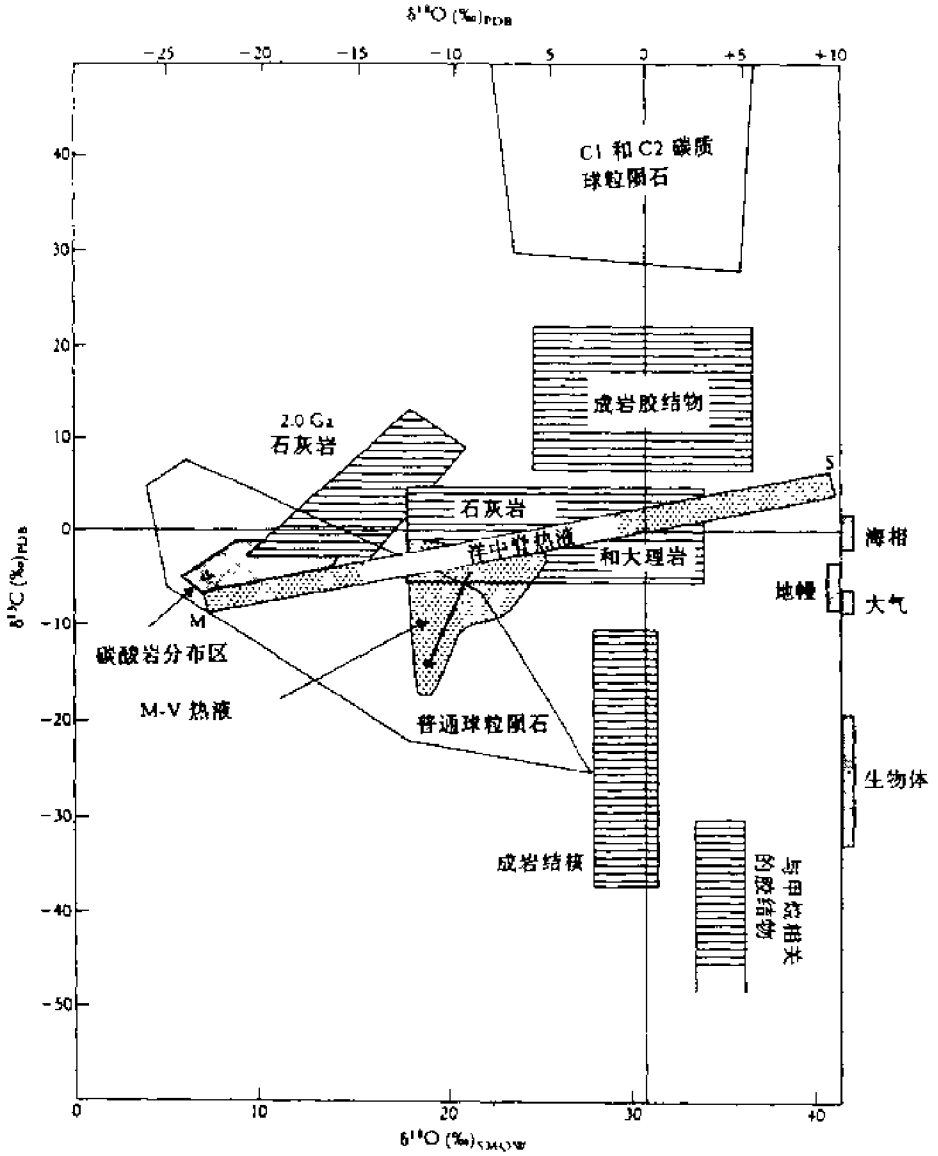


图 7.19 各种环境中碳酸盐的$\delta^{18}O$-$\delta^{13}C$ 组成投影图解。注意$\delta^{18}O$ 同时相对于 SMOW 和 PDB 标准进行了投影。若干不同的碳储库沿图的右手边框作了投影。沉积碳酸盐数值(水平横条)引自 Hudson(1977)和 Baker 等(1989)；洋中脊热液方解石(圆点花纹)呈现幔源碳(M)和海水碳(S)的混合特点(Stakes and O'neil，1982)；在密西西比河谷型矿床(M-V 热液型)的热液方解石分布区中箭头表示年轻化的方向(Richardson 等，1988)。未加修饰的分布区表示陨石的同位素组成(Wright 等，1988)。碳酸岩区据 Deines 和 Gold (1973)。

1. 石灰岩成岩作用

$\delta^{18}O$-$\delta^{13}C$ 图解对理解沉积岩的形成过程特别有用，尤其是对石灰岩的成岩作用。碳同位素研究可以确定碳的来源，区分海相、有机和与甲烷有关的碳(Coleman 和 Raisewell，1981)。沉积碳酸盐氧同位素研究可以用来确定与碳酸盐平衡的流体的来源，利用 Epstein 等(1953)的温度计可以估计碳酸盐形成时的温度。这一温度可能是初始海水的温度或者成岩温度，尽管

建立化学平衡时需要格外小心(McConnaughey，1989)。如果已知温度，则可以计算与方解石胶结物平衡的孔隙水的同位素成分。

Hudson(1977)在一篇关于评论碳 c 和氧同位素在石灰岩成岩作用中应用的论文中，指出不同结晶形态碳酸盐的生长时间是不同的。因此，了解石灰岩成岩作用的最富成效的方法就是分析不同世代的碳酸盐。这将有助建立$\delta^{18}O$-$\delta^{13}C$ 图解上的演化曲线，说明岩石的$\delta^{18}O$-$\delta^{13}C$ 演化历史。习惯上，利用与牙医和珠宝商相似的小钻来分离细小的结晶质共生矿物。然而，激光探针的使用提供了更好的空间分辨 (Smalley 等，1989)。图 7.20 展示了许多“典型”石灰岩同位素的历史演化特征。

Alean 和 Matthews(1980)研究表明，石灰岩和雨水的相互作用可以在$\delta^{18}O$-$\delta^{13}C$ 投影图上得以认识。这种过程的一个特征性指纹就是$\delta^{13}C$ 数值变化范围很大，而$\delta^{18}O$ 值则变化范围较小。造成这种型式的原因是重结晶的碳酸盐的$\delta^{13}C$ 数值是出于两个碳储库的联合(来源土壤的 CO_2 和初始碳酸盐)，而氧同位素则主要由一个雨水储库所控制。

形成于海水与雨水混合的地下水混合带的碳酸盐，对于同一世代的碳酸盐胶结物来说，它们的$\delta^{18}O$ 和$\delta^{13}C$ 数值是典型的正相关关系(Allan 等，1982)。这种正相关关系起因于成分不同的雨水和海水的混合。相对于海水来说，雨水亏损 ^{18}O，当它一旦通过土壤，便会使其 ^{12}C 得到富集。Searl 于(1988，1989)利用这一关系识别南威尔士下石炭统石灰岩中混合带白云岩。

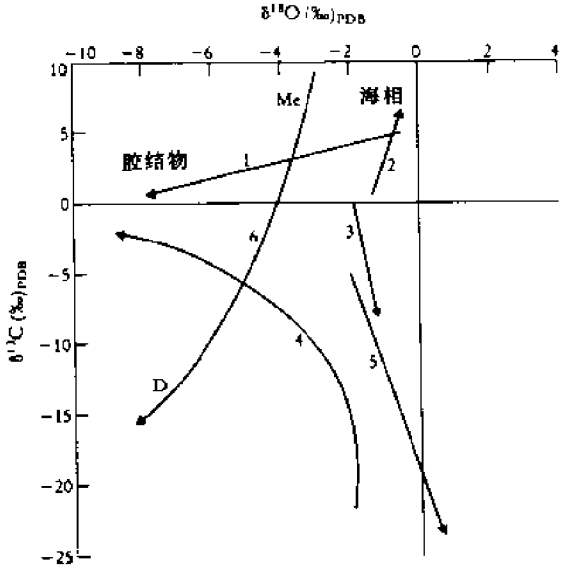


图 7.20　$\delta^{18}O$-$\delta^{13}C$ 投影图，说明成岩石化作用过程中石灰岩和钙质泥岩的同位素演化。变化趋势说明如下：1.石灰岩的成岩固化作用，成分落在初始海水组分(海相)和碳酸盐胶结物之间的混合线上；2.现代海相石灰岩的成岩固化作用呈现$\delta^{13}C$ 的富集伴以$\delta^{18}O$ 轻微的减小，重碳同位素的富集可能是由于光合作用后碳残留的缘故；3.与有机碳相互作用，最大可能是与来源于土壤的 CO_2 的相互作用；4.泥质岩钙质固结物同位素的变化，起因于甲烷的形成以及它们与孔隙水之间的相互关作用；5.碎屑沉淀物中含甲烷成因的碳酸盐；6.在甲烷成因(Me)中和递进缺氧成岩作用的脱碳带(D)(decarboxyeation)泥岩中晚期成岩胶结物的成分变化(数据引自 Hudson，1997 以及 Scotchman，1989)

2. 热液方解石

在$\delta^{18}O$-$\delta^{13}C$ 图解上，处于洋中脊由水-岩相互作用形成的热液方解石表现为宽广的同位素组成(图 7.19)，主要为不同的水/岩比值的函数(Stakes 和 O'Neil，1982)。在一个极端情况下，绿岩角砾中方解石具有与地幔相同的$\delta^{13}C$ 数值，形成于高温(145°C ~ 170°C)下以岩石占主导的环境(低的水 / 岩比值)。低温方解石脉具有海水的$\delta^{13}C$ 数值，表明大量海水与寄主玄武岩发生了相互作用。

Illinois 石炭统石灰岩中，与密西西比河谷型铅-锌成矿作用有关的方解石表现为在其生长的过程中，其$\delta^{13}C$ 数值明显下降，而$\delta^{18}O$ 只以微小的降低(图 7.19)。这些变化表明早期方解石的成分与石灰岩中的碳酸盐非常相似，而在热液体系演化的晚期，与有机碳的退化相关的流体则变得重要(Richardson 等，1988)。

3. **碳酸岩**

碳酸岩的$\delta^{13}C$ 数值的变化范围比$\delta^{18}O$ 值要小得多，在-2‰~8‰(PDB)之间。碳是地幔的一个次要元素，其分布可能不均匀。从石陨石、镁铁质和超镁铁质包体、新鲜玄武岩和金刚石的碳同位素组成来看，$\delta^{13}C$ 数值的变化范围还是较大的。金刚石的$\delta^{13}C$ 数据当然是最可靠的。碳酸岩的$\delta^{13}C$ 数值与金刚石的平均$\delta^{13}C$ 数值相一致，但是后者的变化范围要更大一些(Deines，1989)。

通常，碳酸岩的$\delta^{18}O$ 和$\delta^{13}C$ 数值之间并不存在相关性，但是在$\delta^{18}O$ 数值为 5.5‰~14.5‰范围内，相应的$\delta^{13}C$ 的平均数值从-5.5‰~-2.5‰，存在着微弱的相关性(Deines，1989)。原生的幔源碳酸岩中共生的方解石和白云石具有非常相似的碳和氧同位素组成。然而，有些碳酸岩具有很高的$\delta^{18}O$ 数值，说明它们和地下水可能进行了相互作用，或者经历了重结晶作用(Sheppard 等，1973)。所以，这些碳酸岩显示了次生蚀变的证据。

三、海水的$\delta^{13}C$ 组成

由定义可知，海水的$\delta^{13}C$ 数值接近于 0‰，海相碳酸盐的$\delta^{13}C$ 数值介于-1‰~+2‰之间。然而，古代海水都没有这种恒定的组成，Veizer 等(1986)和 Hoffman 等(1991)业已注意到在元古代记录中海水对现代数值的偏差达到最大值，高达 6‰(PDB)。我们已注意到白垩纪的较小偏差(4.8‰)可用来作为地层学标志。

海水的一些异常$\delta^{13}C$ 数值代表了局部条件；而另一些被认为代表全球的缺氧事件，在这些事件中轻的有机碳汇集到黑色页岩中，导致与之平衡的海水重碳酸盐中$\delta^{13}C$ 相应的得到增加。Baker 等(1989)描述了元古代 (大约 2.0 Ga)期间$\delta^{13}C$ 与海水的巨大的正偏差(13‰ PDB)。这个特征似乎具有世界范围的意义(图 7.19)。这一事件可能记录了光合作用和细菌数量的大量增加。

四、生物地球化学演化

Schidlowski (1987，1988)说明了如何利用地质记录的沉积碳的两个主要形式——碳酸盐和有机碳的碳同位素研究来示踪古代生物活动。他的论点是依据实际观察的结果，生物碳在同位素上是轻的，而碳酸盐则富重的同位素，二者构成互补的碳储库。它们起因于地幔碳的生物分馏作用。因此，这两种储库对应于生物活动水平的变化。在一张说明随时间而变化的碳酸盐和有机碳$\delta^{13}C$ 的变化范围和平均数值图解上，Schidlowski 论证了一旦考虑到成岩作用和变质作用的效应，现在的$\delta^{13}C$ 与 3.8 Ga 最早的地质记录的数值几乎没有变化。他认为这是自从 3.8 Ga 以来生物活动的恒定性以及自从那时起就存在固化 CO_2 的生物作用的有力证据。

五、CO_2 的碳同位素

由于 CO_2 是火成的、变质的和成矿流体的重要组分，所以利用碳同位素组成示踪 CO_2 的

来源具有十分重要的地球化学意义。这类研究多集中在流体包裹体中的 CO_2 以及形成于与富 CO_2 平衡的碳酸盐矿物。从图 7.18，根据$\delta^{13}C$ 值，我们可以区别那些来源于有机碳、地幔和海洋碳酸盐的 CO_2。不幸的是，同位素分馏作用使得这种简单的区分复杂化，很难获得 CO_2 成因唯一的答案。我们在下面将会用一些例子加以说明这个问题。

1. **溶解在火成熔体中的 CO_2**

最近已经认识到从岩浆中离解出来的 CO_2 是评价地幔 CO_2 的重要途径。对大洋玄武岩的分步加热实验得到两部分 CO_2：温度低于 600°C 时，释放出的 CO_2 的$\delta^{13}C$ 值约为−25‰；高于 600°C 时，释放出的 CO_2 的$\delta^{13}C$ 值介于−5‰～−8‰(Javoy，1986)。实验还表明，在 1200 °C 时，碳同位素在溶解于玄武岩浆的碳与 CO_2 之间的分馏约 4‰。在低温下轻的碳同位素特征可能有两种解释：(1)说明是有机碳的混染；或者(2)是 CO_2 分馏和去气作用之后的残余。

2. **变质流体中的 CO_2**

在变质作用过程中，海相石灰岩的去碳酸盐化(脱 CO_2 作用)，导致方解石的$\delta^{13}C$ 值降低(变得更负)(Nabelek 等，1984)，而 CO_2 却相应的富集 ^{13}C。另一方面，生物成因的非碳酸盐的碳的变质作用，导致甲烷的释放，因此残留碳或者石墨的$\delta^{13}C$ 值增大。

1) 麻粒岩

麻粒岩成因的一个流行的解释模型是，麻粒岩是在地壳深部 CO_2 渗透进入的条件下形成的。这个模型是根据许多麻粒岩含有丰富的 CO_2 流体包裹体所建立起来的。Jackon 等(1988)分析了印度南部麻粒岩的富 CO_2 流体包裹体，发现其$\delta^{13}C$ 值介于−5‰～−8‰(PDB)。这个结果说明 CO_2 可能为地幔来源的，尽管相似的$\delta^{13}C$ 值(+2‰10‰)也可以在下地壳的变质作用过程中通过海相碳酸盐的去碳酸盐化而获得(Wickham， 1988)。

2) 变质石墨的成因

变质石墨形成于含碳流体的渗透、与之反应和混合作用。例如，Rumble 等(1986)在 New Hampshire 的高级片麻岩中发现了热液脉状石墨，是由两种流体的混合作用而形成，其中的一种流体含有生物源碳，而另一种流体含有碳酸盐碳。Baker (1988)发现 Ivrea 带泥质岩中通常含有生物源的石墨，但是附近的大理岩体中较高的$\delta^{13}C$ 值说明某些石墨可能源于大理岩的流体。

3. **金成矿流体中的 CO_2**

碳酸盐矿物与太古代脉状金矿床相共生，说明含金成矿流体具有富含 CO_2 的特征。这也是含金流体来源的标志。现在有两种说法，一种认为富含 CO_2 流体为变质成因的，另一种倾向于地幔成因的。利用碳同位素有可能解决这一矛盾。Burrows 等 (1986)发现方解石的平均$\delta^{13}C$ 值介于−3‰～−4‰(PDB)之间。由于只有局部源的碳是偏离海水的(0‰)，因此这些作者提出富 CO_2 流体是外源的和地幔成因的。然而，Groves 等 (1988)的研究工作表明，运用$\delta^{13}C$ 值作为示踪剂存在一些致命的缺点。他们报道了成矿地区存在第二个碳储库，其$\delta^{13}C$ 值接近于那些成矿作用所记录的$\delta^{13}C$ 值(中值为−4‰)。他们的结论是含金流体中 CO_2 是变质成因的，尽管最初来源于地幔并沉淀于断裂带中，它在随后的变质作用中被活化出来。

4. **CO_2 流体/岩石相互作用**

在水/岩相互作用一节中，我们已经讨论了流体/岩石相互作用，其原理也可以用于考虑富 CO_2 流体。当流体/岩石比值小的时候，岩石的$\delta^{13}C$ 在体系中占主导地位，也是变化的流体成分；而当流体/岩石比值大的时候，CO_2 的$\delta^{13}C$ 占主导地位，那么岩石的$\delta^{13}C$ 值就被调整。根据质量平衡限制进行的计算，需要碳酸盐和流体的初始$\delta^{13}C$ 数值，含碳离子的比例以及 CO_2

与含碳离子之间的$\delta^{13}C$ 分馏系数(图 7.21)。方解石和石墨的初始$\delta^{13}C$ 值和漂移到现在的测定值，可以来计算流体-岩石相互作用的程度。Baker (1988)和 Kreulen (1988)给出了良好的计算实例。Baker 发现 Ivrea 带的角闪岩和麻粒岩相岩石中流体/岩石比值非常低，而 Kreulen 发现 Naxos 片岩的流体-岩石比值高达 2.0。

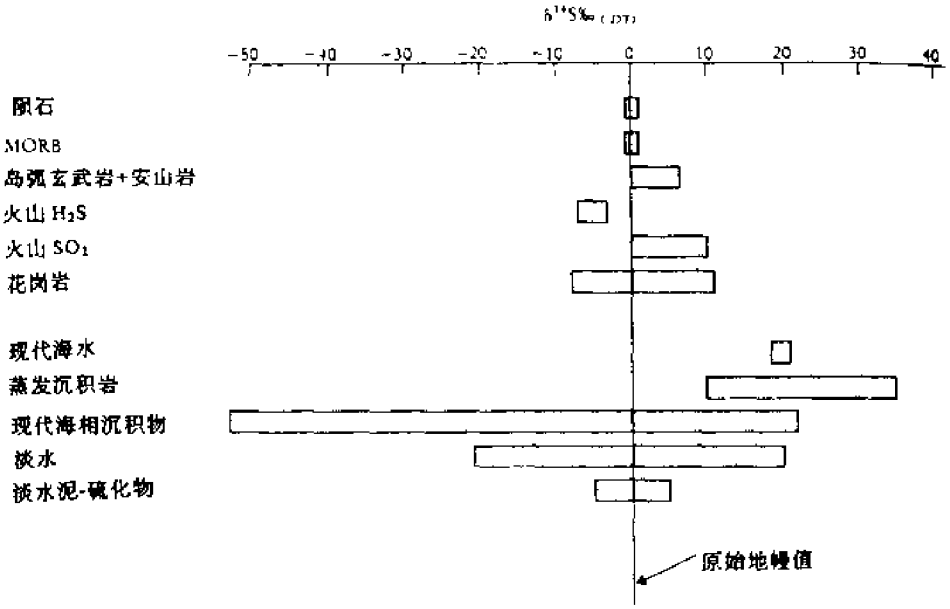


图 7.21 和表 7.2 说明$\delta^{13}C$ 在不同碳的物相之间的分馏作用在许多情形下与温度密切相关。其中的两种分馏作用已经用于作为测定变质岩温度的温度计。

六、碳同位素温度计

1. 方解石-石墨$\delta^{13}C$ 温度计

在许多变质岩中，石墨与方解石共生。这是一种潜在的温度计，适用温度范围为 600°C 以上。目前使用的校正方法有 3 种。Bottinga (1969)的校正方法基于理论计算，适用的温度范围最宽。Valley 等 (1981)根据二长石和钛铁矿-磁铁矿温度计计算的温度(在 600° C ~ 800°C 范围内有效)提出了一种经验性校正。这个曲线比 Bottinga (1969)的计算曲线约低 2‰。Wada 等(1983)利用白云石-方解石固溶线温度计得到的温度也校正了方解石-石墨和白云石-石墨温度计。他们的校正在 400° C ~ 680° C 范围内有效，并在高温下接近于 Valley 等 (1981)的结果。Valley 等(1981)指出温度低于 600°C 时方解石与石墨间达不到同位素平衡。然而，当温度高于 600°C 时，方解石中的有机碳则丧失其特征的负的$\delta^{13}C$ 指纹。

2. CO_2-石墨温度计

流体包裹体 CO_2 的碳同位素组成及其与之共生的石墨的碳同位素组成也可用作温度计。Bottinga(1969)校正了这种交换，参见图 7.18。Jackson 等(1988)使用的方法所获得的平衡温度接近于从印度南部麻粒岩相片麻岩中石英及石墨中富 CO_2 流体包裹体获得的变质作用高峰温度。

以下是控制$\delta^{13}C$ 分馏作用的方程(除了特别说明外，温度单位为 K)：

CO_2 方解石 (Bottinga，1969) (0°C~700°C)

$$1000\ln\alpha=-2.998(10^6/T^2)+7.6663(10^3/T)-2.4612$$

白云石-方解石 (Sheppard 等，1970) (100°~650 °C)

$$1000\ln\alpha=0.18(10^6/T^2)+0.17$$

方解石-石墨 (Valley 等，1981) (610°C~760 °C)

$$\Delta_{方解石-石墨}=0.00748T+8.68 \text{ (温度以°C 为单位)}$$

方解石-石墨 (Wada 等，1983)(400°C~680 °C)

$$\Delta_{方解石-石墨}=5.6(10^6/T^2)-2.4$$

白云石-石墨 (Wada 等，1983)(400°C~680 °C)

$$\Delta_{白云石-石墨}=5.9(10^6/T^2)-1.9$$

第五节　硫同位素的应用

自然界的硫具有 4 种同位素，它们的丰度为：^{32}S=95.02%，^{33}S=0.75%，^{34}S=4.21%，^{36}S=0.02%。在地球化学中常利用两种丰度最大的硫同位素比值 $^{34}S/^{32}S$，相对于 Canon Diablo 铁陨石中陨硫铁(CDT)标准样，求千分值，表示为：

$$\delta^{34}S(‰)=\left[\frac{^{34}S/^{32}S_{(样品)}-^{34}S/^{32}S_{(标准)}}{^{34}S/^{32}S_{(标准)}}\right]\times 1000 \qquad [7.17]$$

硫同位素的测定是把待测样品制备成 SO_2 气体，在质谱计上进行测量的精度约 0.02‰，准确度约为 0.10‰。现在利用离子探针可以直接测定细 c 粒硫化物变生体的硫同位素比值，其精度介于 1.5‰ ~ 3.0‰之间(Eldridge 等，1988)，而激光探针的分析精度为 ± 1.0‰。表示硫同位素数据的最常用方式是频率-直方图。双变量相关图解很少用来描述硫同位素数据，但是有时总硫投影图是非常有意义的。

一、硫同位素在自然界的分布

在自然界出现的含硫物种包括自然硫、硫酸盐和硫化物矿物、气相以及溶液中氧化态和还原态硫离子。图 7.22 总结了一些主要岩石类型的硫同位素组成。

现有三种不同的$\delta^{34}S$ 储库：幔源硫，其$\delta^{34}S$ 值约为 0 ± 3‰(Chaussidon 等，1990)；现在的海水硫，其$\delta^{34}S$ 值为+20‰，但是这个数值在过去可能是变化的；以及具有$\delta^{34}S$ 大的负值的强烈还原(沉积的)硫。原始地幔相对于 CDT 的$\delta^{34}S$ 最佳估计值为 0.5‰(Chaussidon 等，1989)，与球粒陨石略有不同(0.2 ± 0.2‰)。MORB 数值是亏损地幔的代表，具有狭窄的变化范围：+3 ± 0.5‰ (Sakai 等，1984)。岛弧火山岩石具有较宽的$\delta^{34}S$ 值变化范围(-0.2‰ ~ +20.7‰)、花岗质岩石的$\delta^{34}S$ 值变化也非常大(-10‰ ~ +15‰)，与 Chaussidon 等(1989)提出的平均大陆地壳($\delta^{34}S$ = +7.0‰)相比具有较宽的值变化范围。

二、硫同位素分馏的控制因素

图 7.21 表明许多地壳岩石具有宽广的$\delta^{34}S$ 值变化范围，说明它们经过了广泛的分馏作

用，这些分馏机制将在以下进行概括。

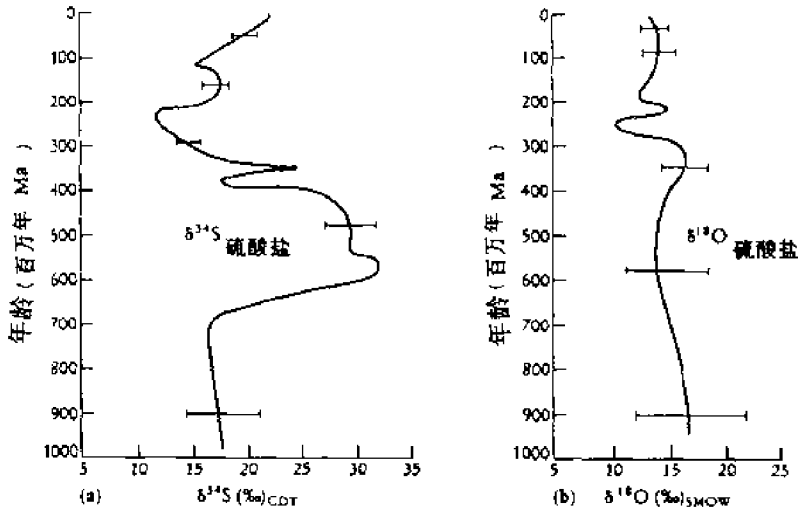


图 7.22 天然硫同位素储库。数据引自：Sakai 等，1982；Ueda 等，1984；Claypool 等，1980； Kerridge，1983；Chambers，1982；Coleman，1977；Claussidon，1989；图 7.28 也给出了相似的含硫热液矿物图解。

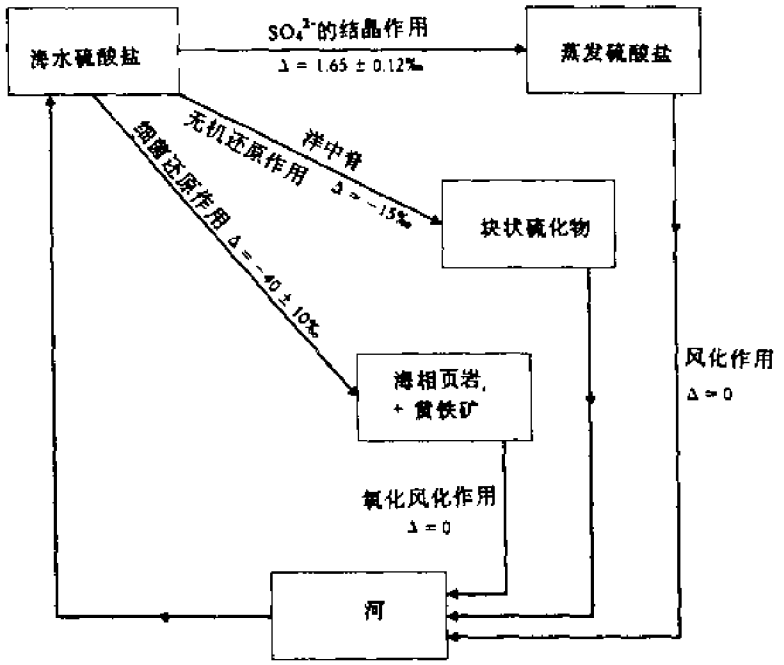


图 7.23 与海水平衡的硫酸盐的$\delta^{34}S$和$\delta^{18}O$值随时代的变化曲线；$\delta^{34}S$ 相对于 CDT，而$\delta^{18}O$相对于 SMOW。曲线反映蒸发盐矿床中硫酸盐的同位素组成，误差线段表示不同时间间隔的不确定性。氧同位素组成曲线的制约比硫同位素曲线要差一些。$\delta^{34}S$ 在溶解于海水的硫酸盐与蒸发硫酸盐之间的分馏是 1.65‰。因此，严格地说，这一数值应从给定的数值中减掉。然而，相对小的差异处于投影曲线误差之内，通常被忽略了。另一方面，$\delta^{18}O$ 在海水与蒸发硫酸盐之间分馏为 +3.5‰，因此，为了获取一定时代的海水中硫酸盐的$\delta^{18}O$ 成分，应从投影值中扣除+3.5‰(据 Claypool 等，1980)。

1. 火成岩中硫同位素的分馏作用

火成熔体中硫同位素分馏是较小的，发生于晶体与熔体之间，或者通过固-气分馏作用。原生硫化物与岩浆之间的$\delta^{34}S$ 分馏为 1‰~3‰量级(Ohmoto 等，1979；Chaussidon 等， 1989)。分异的长英质和镁铁质序列岩石所记录的最大的$\delta^{34}S$ 值的降低为 1‰(Ueda 等，1984)。

火成岩中硫同位素分馏的另一个途径是通过次空间或浅亚海相熔岩的 SO_2 去气作用。这

种分馏作用受到熔体的硫酸盐/硫化物比值控制，同时也受控制于温度、压力、水含量和氧逸度。基性熔岩去气的 SO_2 相对于熔体而言，具有富$\delta^{34}S$ 的特点，因为在熔体占主导的硫物种是硫化物，SO_2 相对于硫化物富集$\delta^{34}S$(见图 7.23)。这种过程从夏威夷的 Kilauea 火山得到并记录下来(Sakai 等，1982)，Zheng(1990)作了定量研究。

2. 沉积岩中硫同位素的分馏

沉积硫循环及其相伴的$\delta^{34}S$ 分馏总结于图 7.24。有以下四种可能的过程。

1) 细菌还原作用使硫酸盐变为硫化物

低温控制(即低于 50°C)硫同位素分馏主要是海水硫酸盐还原为沉积硫化物，尽管有证据表明这一过程并不发生在太古代期间(Hattori 等，1983)。这一反应受动力学控制，因为业已证实较轻的离子 $^{32}SO_4^{2-}$的反应速率比较重的 $^{34}SO_4^{2-}$离子快 2.2‰(Harrison 等，1957)。因此，这类反应进行到底将造成硫化物相对于海水源区亏损 22‰。

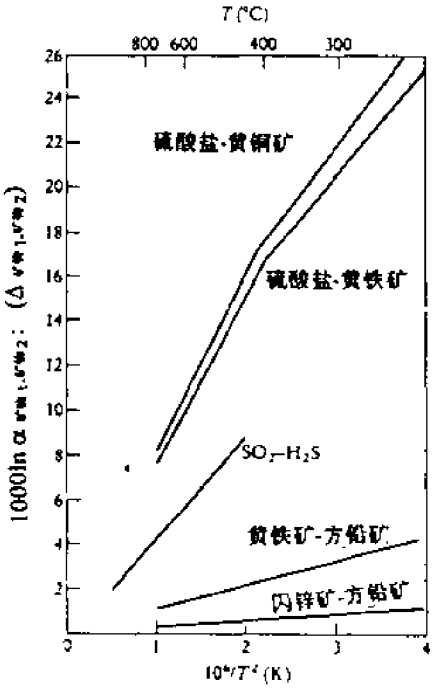


图 7.24 ^{34}S 在矿物对之间及在 H_2S-SO_2 间的分配作为温度的函数。这些分馏曲线可以用来当作硫同位素温度计，表明最大的分馏存在大于硫化物和硫酸盐矿物之间。

除了考虑沉积硫化物分馏的动力学控制之外，考虑体系是否开放或者封闭的也十分重要。在这样一个巨大的停滞的海水体开放体系中，具有一个无限的海水硫酸盐储库。发生在停滞的低层水中的硫酸盐的细菌还原作用将产生 ^{34}S 极度亏损的 H_2S，而海水储库的$\delta^{34}S$ 则没有明显的变化。Chamber(1982)报道了现代潮间沉积物的分馏高达 48‰。在一个封闭体系中，硫化物的分离是通过 H_2S 气体的丢失或硫化物矿物的沉淀而实现的，硫同位素分馏受 Rayleigh 分馏控制，Ohmoto 等(1979)给出了分馏方程。在这种情况下，硫酸盐的同位素组成也是变化的；而随着硫酸盐含量的减少，残留的硫酸盐则具有非常高的$\delta^{34}S$ 值(见 Richardson 等(1988)给出的实例)。

2) 细菌氧化作用使硫化物变为硫酸盐

与海水硫酸盐的细菌还原作用不同，硫化物的细菌氧化作用产生非常小的分馏作用，是不重要的，但是也许太古代的情况例外(Hattori，1989)。

3) 沉积硫酸盐从海水中的结晶作用：蒸发岩的形成

在蒸发盐形成过程中，沉积硫酸盐的结晶作用产生了相对小的$\delta^{34}S$ 富集作用，约为 1.65 ± 0.12‰ (Thode 等，1965)。

4) 非细菌还原作用使硫酸盐变为硫化物

一些矿床的研究表明，含硫酸盐溶液在温度高于硫酸盐还原细菌的条件下经还原作用可以形成硫化物，说明存在硫酸盐的无机还原作用(Trudinger 等，1985)。有两种可能的过程。当温度为 75°C~175°C，无机硫酸盐还原作用可能发生于碳氧化物存在的条件下。这种变异可能是含硫有机化合物的分解，形成与煤伴生的硫化物(Whelan 等，1988)。当温度高于 250°C，硫酸盐还原可能通过与二价铁的还原作用而得到。这一过程在海水与 MORB 相互作用中尤其重要(见本章第四节)。

3. 热液体系中的硫同位素分馏

在高温(T>400°C)条件下，热液体系中硫的主要物种是 H_2S 和 SO_2，热液的硫同位素可近似为：

$$\delta^{34}S_{流体}=\delta^{34}S_{H_2S}X_{H_2S}+\delta^{34}S_{SO_2}X_{SO_2} \qquad [7.18]$$

其中 X_{H_2S} 是流体中 H_2S 相对于总硫的摩尔分数，X_{SO_2} 为 SO_2 的摩尔分数 (Ohmoto 等，1979)。在这种温度条件下，H_2S 和 SO_2 的行为被假设为理想气体混合物。分馏系数数值由表 7.4 给出。图 7.25 给出了分馏曲线。

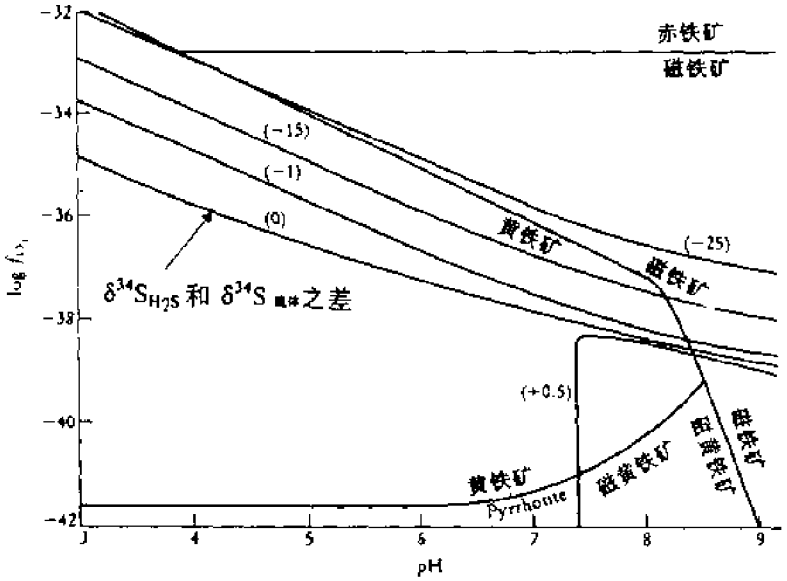


图 7.25 硫同位素的 Logf_{O_2} 对 pH 图解，并表示黄铁矿、磁黄铁矿、磁铁矿和赤铁矿稳定场。边界的μ=1.0，总硫摩尔浓度=0.01，K^+=0.1，Na^+=0.9，Ca^{2+}=0.01。那些标有数值的曲线表示在 250°C 平衡条件下$\delta^{34}S_{H_2S}$ 对$\delta^{34}S_{流体}$的偏离

在较低的温度(T<350°C)条件下，热液体系中硫以硫酸盐和 H_2S 为主 (Ohmoto 等，1979)，所有硫酸盐物种假设具有相同的分馏系数，这些也由表 7.4 给出了。Ohmoto 等(1979)总结了大量非常重要的研究成果，表明热液流体中不同含硫物种之间的$\delta^{34}S$ 分馏并不简单地受温度控制，而是流体的物理-化学条件的函数：这些包括氧逸度、硫浓度、pH 和与硫酸盐有关的阳离子的活度。这种效应用 log(氧逸度)对 pH 图解来表示(图 7.26)，说明若干相关矿物相的稳定场关系。从热液流体中沉淀的矿物的$\delta^{34}S$ 对其流体的$\delta^{34}S$ 偏离是氧逸度和 pH 的函数。这个图解预测：形成于与磁铁矿平衡的硫化物矿物的$\delta^{34}S$ 值将比热液的低得多；而在低氧逸度和 pH 条件下，流体与矿物将具有相近的$\delta^{34}S$ 数值。

这一研究的重要性，首先是明确了热液流体的$\delta^{34}S$ 不能直接由从中沉淀的硫化物的$\delta^{34}S$ 值来估算，除非已知氧逸度和 pH 等变量。其次，硫化物矿物不能直接用来确定热液流体中硫的来源，因为它是许多变量(不单是温度)的函数。

4. 硫化物与硫酸盐间的硫同位素分馏：硫同位素温度计

共生硫化物之间的$\delta^{34}S$ 分馏作为温度的函数，已有许多理论和实验的结果(表 7.4)，由这些结果所获得的硫化物矿物对温度计由表 7.5 和图 7.26 给出。然而，硫同位素在硫化物之间的分配并不是一个十分灵敏的温度计，需要精确地测定其同位素组成，更广泛的$\delta^{34}S$ 分馏则发生在硫化物和硫酸盐矿物相之间。

硫化物矿物对和硫化物-硫酸盐矿物对之间并不总是处于平衡。这种情况发生于(1)矿物对

形成于低温条件(T<200°C)；(2)成矿流体的同位素成分是变化的；(3)随着矿物相形成之后，存在不断的同位素交换。同位素是否得到平衡可以通过测定共生矿物的温度来得到证明。两个温度若一致，则可以作为共生矿物已达到同位素平衡的证据。

表 7.4 ^{34}S 在 H_2S 和硫化物之间的分配。控制方程为 $1000\ln\alpha_{sulfide-H_2S} = A(10^6/T^2)+B$(温度的单位是 K)

矿物	A	B	温度范围(°C)	参考文献
硬石膏/石膏	6.463	0.56	200~400	Ohmoto 等(1982)
重晶石	6.5 ± 0.3		200~400	Miyoshi 等(1984)
辉钼矿	0.45 ± 0.1		不确定	Ohmoto 等(1979)
黄铁矿	0.40 ± 0.08		200~700	Ohmoto 等(1979)
闪锌矿	0.1 ± 0.05		50~705	Ohmoto 等(1979)
磁黄铁矿	0.1 ± 0.05		50~705	Ohmoto 等(1979)
黄铜矿	-0.05 ± 0.08		200~600	Ohmoto 等(1979)
辉铋矿	-0.67 ± 0.07		250~600	Bente 等(1982)
方铅矿	-0.63 ± 0.05		50~700	Ohmoto 等(1979)
SO_2	4.70	-0.5 ± 0.5	350~1050	Ohmoto 等(1979)

表 7.5 根据分馏系数(表 7.4)进行的硫同位素温度计校正(温度的单位为 K)

矿物对	分馏系数方程		参考文献
黄铁矿-方铅矿	$1000\ln\alpha=1.03\ (10^6/T^2)$		Ohmoto 等(1979)
	$1000\ln\alpha=1.08\ (10^6/T^2)$	(150°~600°C)	Clayton(1981)
黄铁矿-闪锌矿(黄铁矿-磁黄铁矿)	$1000\ln\alpha=0.3\ (10^6/T^2)$		Ohmoto 等(1979)
黄铁矿-黄铜矿	$1000\ln\alpha=0.45\ (10^6/T^2)$		Ohmoto 等(1979)
闪锌矿-方铅矿(磁黄铁矿-方铅矿)	$1000\ln\alpha=0.73\ (10^6/T^2)$		Ohmoto 等(1979)
	$1000\ln\alpha=0.76\ (10^6/T^2)$	(100°~600°C)	Clayton(1981)
硫酸盐-黄铁矿	$1000\ln\alpha=6.063\ (10^6/T^2)$		Ohmoto 等(1982)
硫酸盐-黄铜矿	$1000\ln\alpha=6.513\ (10^6/T^2)$		Ohmoto 等(1982)

三、硫同位素在火成成因岩石学中的运用

本节给出三个例子来说明解释火成岩的硫同位素组成的不同方法。

1. SO_2 的去气作用

Kilauea 火山近地表的硫同位素成分与亚海相熔岩的硫同位素成分存在着明显差异(Sakai 等，1982)，这可能归因于 SO_2 去气作用。亚海相玄武岩具 $\delta^{34}S$=+0.7‰和高的硫酸盐-硫化物比值，而近地表玄武岩却含有低的总硫和还原的 $\delta^{34}S$ (–0.8‰)及低的硫酸盐-硫化物比值，所有这些特征与 SO_2 的快速去气作用十分一致。这一机制也被 Faure 等(1984)和 Mensing 等(1984)所推崇，他们发现了 Antaretica 侏罗纪 Kirkpatrick 玄武岩具有宽的 $\delta^{34}S$ 值范围(–1.45‰–11.73‰)。在这些岩石中，$\delta^{34}S$ 与磁铁矿含量相关，磁铁矿是高氧逸度的标志矿物。因此，Faure 等(1984)提出高氧逸度促使 SO_2 作为主要硫的稳定形式及去气，引起玄武岩变化范围大的 $\delta^{34}S$ 数值。

2. 混染作用

Mariana 岛屿的玄武岩-安山岩-英安岩套的$\delta^{34}S$ 值变化于+2‰~+20.7‰之间。这一相对于地幔值的巨大变化范围可能反映岩浆受到了海相硫酸盐的混染(Woodhead 等，1987)。

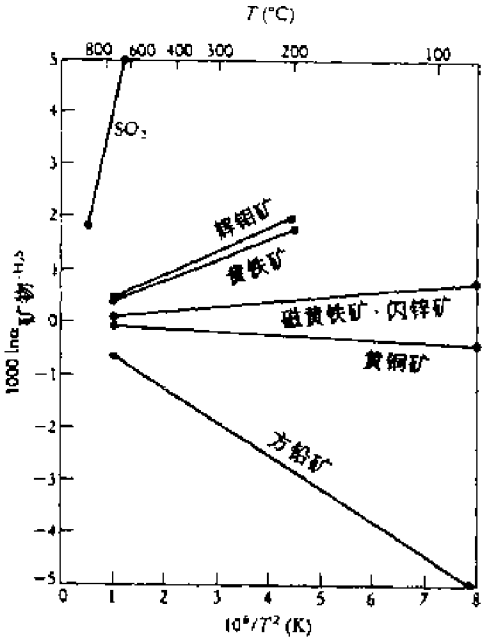


图 7.26 ^{34}S 在矿物与 H_2S 之间的分配是温度的函数。这些分馏曲线被用以作为表 7.4 给出的硫同位素温度计的基础。在图解中分开最大的矿物对将是最灵敏的温度计(Ohmoto 等，1979)。

3. 晶体分离作用

苏格兰东北的 Huntley-Knock 侵入体中的层状辉长岩含有岩浆成因的硫化物水平层。堆积岩中硫化物的$\delta^{34}S$ 值平均为 0.5‰，接近于地幔值(Fletcher 等，1989)。然而，侵入体内的$\delta^{34}S$ 值从接触带(平均值为-1.2‰)到堆积岩和粒状岩石(平均为+2.4‰)的不同部位发生了明显变化。这个变化可以归因于在氧逸度变化条件下的岩浆同位素分馏作用。

四、硫同位素在热液矿床成因研究中的运用

热液矿床的硫同位素研究可以获取以下信息：(1)确定硫的来源；(2)确定硫化物及成矿流体的形成温度；(3)确定有效成矿过程中水/岩比值；(4)确定矿物间硫同位素达到平衡的程度；(5)限制矿床的形成机理。

1. 大洋中脊的现代热液成矿作用

发育在现代洋中脊的高温热液脉为研究热液矿床形成过程提供了极好的实例。目前的工作模式是，冷的海水硫酸盐被带进洋底玄武岩之中，并被附近的岩浆房所加热。一些硫酸盐以硬石膏的形式沉淀下来，而其余的通过与玄武岩反应被还原为硫化物。温度为 150°C 的热液流体携带硫化物沿着裂隙返回海底。这种流体与海水混合，在海底沉淀出细粒的硫化物沉淀物，而在流体的通道之处，沉淀的硫化物构成高约 1 米的“烟囱”。

东太平洋隆起的研究(Woodruff 等，1988；Bluth 等，1988)确定了该体系不同成分的硫同位素组成(图 7.27)。这些数据可以用来检验上述的模式，这类矿床的许多事实说明：

(1)硫化物矿物之间同位素不相互平衡，因为利用硫同位素测温的结果与热液流体的已知温度不一致。

(2)硫化物矿物相的$\delta^{34}S$ 从烟囱内壁到外壁是变化的。

(3)矿脉流体与沉淀的矿物之间明显没有达到同位素平衡。

(4)脉流体的$\delta^{34}S$ 成分由玄武岩硫与还原的海水硫酸盐的混合作用而形成，其精确值是水/岩比值的函数(Skirrow 等，1982)。

(5)热液流体的成分是变化的。

(6)同生硫酸盐矿物(硬石膏)与海水硫酸盐之间处于平衡。

2. 古代热液成矿作用

Ohmoto(1986)评述了热液矿床的硫同位素成分。图 7.28 总结了一些热液矿床的$\delta^{34}S$ 值，从中可以看出某些类型的矿床具有狭窄的成分范围，因而具有一相当特定的物质来源，而一些矿床则具有宽广的成分范围，物质来源可能是多源的。密西西比河谷型矿床就是这后一类

矿床的实例。密西西比河谷型矿床的硫化物具有如图 7.28 所示的整个成分范围的同位素组成。然而，单个矿床具有相对一定的$\delta^{34}S$ 值变化范围，支持了每种情况下硫的来源和产生的机制是不同的观点。

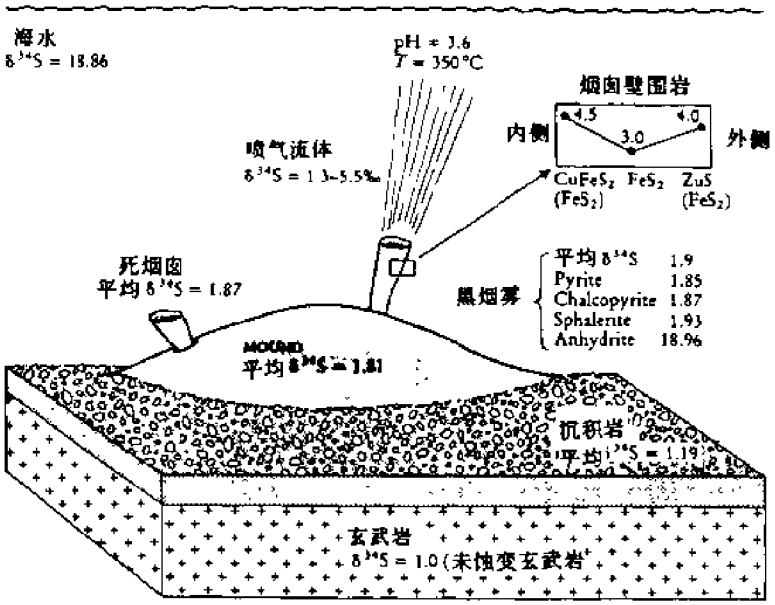


图 7.27 现代洋中脊热液脉的$\delta^{34}S$ 值的图解表示。大多数数值引自 Kerridge 等 (1983)，同时也有引自 Bluth 等(1988)和 Woodruff 等(1988)。放大的烟囱表示$\delta^{34}S$ 值的变化和硫化物成分从烟囱内壁向外壁的变化。Bluth 等(1988)在一个模式中解释了这些特征，流体的$\delta^{34}S$ 值在烟囱的寿命内随着时间而变化，这是由于矿网脉系统之下的玄武岩中热杠和水/岩比变化的结果。此外，热液与已沉淀在烟囱上的硫化物发生反应，导致在烟囱的生长过程中它们成分的变化。

以下简要评述几种不同类型的热液矿床，并按它们可能的硫源进行分类。

1) 海水硫酸盐的高温无机还原作用

这个机制在上面洋中脊块状硫化物矿床的描述中已作了较为详细的讨论。这同样也适用于产于长英质钙-碱性熔岩中的 Kuroko 型块状 Pb-Zn 硫化物矿床。大多数 Kuroko 矿石硫化物的$\delta^{34}S$ 值变化范围为+5‰ ~ +8‰，硫酸盐的$\delta^{34}S$ 值介于 21.5‰ ~ 28.5‰。Kuroko 硫酸盐和现代海水的$\delta^{34}S$ 值的密切关系(Sangster，1968)表明无机硫酸盐还原作用是硫化物形成的一个可能机制。

2) 硫酸盐的低温有机还原作用

在英格兰西北部 Cheshire 盆地中的红层铜矿化与蒸发沉积作用有关。硫化物显示宽的$\delta^{34}S$ 数值(−1.8‰ ~ +16.2‰)，与之共生的重晶石的$\delta^{34}S$ 值变化在 13.8‰ ~ 19.3‰之间。后者的这些数值与上覆层位的蒸发盐硫酸盐的$\delta^{34}S$ 值(18.4‰~20.8‰)相近。Naylor 等(1989)提出重晶石和硫化物由来源于这个源区的含硫溶液而形成。成矿温度还不清楚，但是据认为超过硫酸盐还原细菌能够存在的温度。由于这个原因，作者提出硫酸盐还原作用发生于气体碳氢化合物存在的条件下，在一个封闭体系内还原作用导致硫化物的形成，但是作用进行得不完全。

3) 硫酸盐的低温细菌还原作用

德国 Rammelsberg 矿床是一个赋存在沉积岩中的块状硫化物矿床，主要由含不同比例的黄铁矿、黄铜矿和其它与硅酸盐一起的硫化物的碎块所组成。黄铁矿碎块的$\delta^{34}S$ 值落在三个不同范围(+12‰ ~ +16‰； +3‰ ~ −3‰； −10‰ ~ −17‰)。在频率直方图上，这些数值呈现一个歪斜的分布。这一特征在火山成因的块状硫化物矿石中并未发现，被认为是赋存在沉积岩

中的块状硫化物的特征(Eldridge 等，1988)，低的数值组最容易用部分开放体系中海水硫酸盐(分馏系数约为(–45‰±20‰))的细菌还原作用来解释。较高的$\delta^{34}S$ 值可能是热液来源的，在沉积过程中由两组碎屑混合而成。

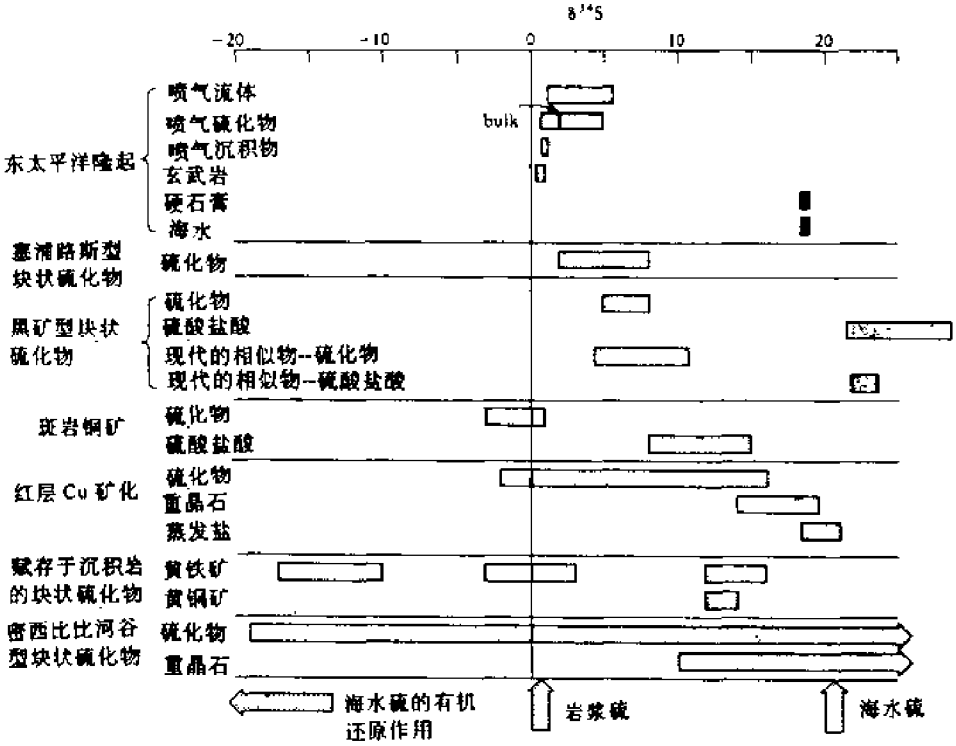


图 7.28 热液矿床含硫矿物的上$\delta^{34}S$ 值。数据引自 Kerridge 等(1988)，Ohmoto 等（1979），Halback 等(1989)，Naylor 等(1989)和 Eldridge 等(1988)。

4) 硫的岩浆成因

斑岩铜矿床的硫是最可能来源于岩浆的代表。硫化物的$\delta^{34}S$ 值落在狭窄的–3‰～+1‰范围内，接近于公认的地幔范围。硫酸盐和硫化物是平衡的，其温度为 450°C～460°C(Ohmoto 等，1979)。此外，氧和氢同位素数据表明计算的流体成分接近于岩浆流体。

参 考 文 献

Abbey S., 1989, The evaluation of reference materials for rock analysis. In: Ahmedali S.T. (ed.), *X-ray fluorescence analysis in the geological sciences: Advances in Methodology*. Geol. Assn. Canada: Short course 7, 1~38.

Adam J., 1988, Dry, hydrous and CO_2-bearing liquidus phase relationships in the CMAS system at 28 kb, and their bearing on the origin of alkali basalts. J. Geol., 96, 709~720.

Addy S.K. and Garlick G.D., 1974, Oxygen isotope fractionation between rutile and water. Contrib. Mineral Petrol., 45, 119~121.

Ahmedali S.T. (ed.), *X-ray fluorescence analysis in the geological sciences: Advances in Methodology*. Geol. Assn. Canada: Short course 7.

Aitchison J., 1981, A new approach to null correlation of proportions. J. Math. Geol., 13, 175~189.

Aitchison J., 1982, The statistical analysis of compositional data (with discussion). J. Roy. Stat. Soc., 44, 139~177.

Aitchison J., 1984, The statistical analysis of geochemical compositions. J. Math. Geol., 16, 531~564.

Aitchison J., 1986, *The statistical analysis compositional data*. Methuen, New York.

Aitchison J., 1989, Measures of location of compositional data sets. J. Math. Geol., 21, 787~790.

Allan J.R. and Matthews R.K., 1982, Isotope signatures associated with early meteoric diagensis. Sedimentology, 29, 797~817.

Allegre C.J., 1987, Isotope geodynamics. Earth Planet. Sci. Lett., 86, 175~203.

Allegre C.J. and Ben Othman D., 1980, Nd-Sr isotopic relation in granitoid rocks and continental crust development: a chemical approach to orogenesis. Nature, 286, 335~342.

Allegre C.J., Hart S.R. and Minster J.-F., 1983a, Chemical structure and evolution of the mantle and continents determined by inversion of Nd and Sr isotopic data, I. Theoretical models. Earth Planet. Sci. Lett., 66, 177~190.

Allegre C.J., Hart S.R. and Minster J.-F., 1983b, Chemical structure and evolution of the mantle and continents determined by inversion of Nd and Sr isotopic data, II. Numerical experiments and discussion. Earth Planet. Sci. Lett., 66, 191~213.

Allegre C.J., Lewin E. and Dupre B., 1988, A coherent crust-mantle model for the uranium-thorium-lead isotopic system. Chem. Geol., 70, 211~234.

Allegre C.J., and Minster J.-F., 1978, Quantitative models of trace element behaviour in magmatic processes. Earth Planet. Sci. Lett., 38, 1~25.

Allegre C.J. and Rousseau D., 1984, The growth of the continents through geological time studied by the Nd isotopic analysis of shales. Earth Planet. Sci. Lett., 67, 19~34.

Allegre C.J., Treuil M., Minster J.-F., Minster B. and Albarede F., 1977, Systematic use of trace elements in igneous processes. Part I: fractional crystallization processes in volcanic suits. Contrib. Mineral Petrol., 60, 57~75.

Allen P., Condie K.C. and Narayana B.L., 1985, The geochemistry of prograde and retrograde charnockite-gneiss reactions in southern India. Geochim. Cosmochim. Acta, 49, 323~336.

Anders E. and Ebihara M., 1982, Solar system abundances of the elements. Geochim. Cosmochim. Acta,46, 2363~

2380.

Anderson J.L. and Cullers R.L., 1987, Crust-enriched, mantle-derived tonalites in the early Proterozoic, Penokean orogen of Wiscosin. J. Geol., 95, 139~154.

Apted M.J. and Roy S.D., 1981, Corrections to the trace element fractionation equations of Hertogen and Gijibels (1976). Geochim. Cosmochim. Acta,45, 777~778.

Arculus R.J., 1987, The significance of source verus process in the tectonic controls of magma genesis. J. Volc. Geothermal Res., 32, 1~12.

Argast S. and Donnelly T.W., 1987, The chemical discrimination of clastic sedimentary components J. Sed. Petrol., 57, 813~823.

Arndt N.T. and Goldstein S.L., 1987, Use and abuse of crust-formation ages. Geology, 15, 893~895.

Arndt N.T. and Jenner G.A., 1986, Crustally contaminated komatiites and basalts from Kambalda, western Australia. Chem. Geol., 56, 229~255.

Arth J.G., 1976, Behaviour of trace elements during magmatic processes—a summary of theoretical models and their applications. J. Res. U.S. Geol. Surv., 4, 41~47.

Arth J.G., 1981, Rare-earth element geochemistry of the island-arc volcanic rocks of Rabaul and Talasea, New Britain. Bull. Geol. Soc. Am., 92, 858~863.

Ayalon A. and Longstaff F.J., 1988, Oxygen isotope studies of diagenesis and pore water evolution in the western Canada sedimentary basin: evidence from the Upper Cretaceous basal Belly River sandstone, Alberta. J. Sed. Petrol., 58, 489~505.

Bailey J.C., 1981, Geochemical criteria for a refined tectonic discrimination of orogenic andesites. Chem. Geol., 32, 139~159.

Baker A.J., 1988, Stable isotope evidence for limited fluid infiltration of deep crustal rocks from the Ivrea Zone, Italy. Geology, 16, 492~495.

Baker A.J. and Fallick A.E., 1989, Evidence from Lewisian limestones for isotopically heavy carbon in two-thousand-million-year-old sea water. Nature, 337, 352~354.

Baker D.R. and Eggler D.H., 1983, Fractionation paths of Atka (Aleutians) high-alumina basalts: constraints and phase relations. J. Volc. Geothermal Res., 18, 387~404.

Baker D.R. and Eggler D.H., 1987, Compositions of anhydrous and hydrous melts coexisting with plagioclase, augite, and olivine or low-Ca pyroxene from 1 atm. to 8 kbars: application to the Aleutian volcanic center of Atka. Am. Mineral., 72, 12~28.

Baker D.S., 1978, Magmatic trends on alkali-iron-magnesium diagrams. Am. Mineral., 63, 531~534.

Baker F., 1979, Trondhjemite: Definition, environment and hypotheses of origin. In: Baker F. (ed.), *Trondhjemites, dacites and related rocks*. Amsterdam: Elsevier , pp.1~12.

Barnes S.-J., 1988, Automated plotting of geochemical data using the Lotus symphony package. Computer Geosci., 14, 409~411.

Barnes S.-J. and Naldrett A.J., 1986, Variations in platinum group element concentrations in the Alexo mine komatiite, Abitibi greenstone belt, northern Ontario. Geol. Mag., 123, 515~524.

Barnes S.-J., Naldrett A.J. and Gorton M.P., 1985, The origin of platinum-group elements in terrestrial magmas.,

Chem. Geol., 53, 303~323.

Barth T.W., 1952, Theoretical petrology: a textbook on the origin and evolution of rocks. New York: Wiley.

Basu A.R., Sharma M. and DeCelles P.G., 1990, Nd, Sr-isotopic provenance and trace element geochemistry of Amazonian foreland basin fluvial sands, Bolivia and Peru: implication for ensialic Andean orogeny. Earth Planet. Sci. Lett., 100, 1~17.

Beach A. and Tarney J., 1978, Major and trace element patterns established during retrogressive metamorphism of granulite facies gneisses, NW Scotland. Precamb. Res., 7, 325~348.

Bell K., Blenkinsop J., Cole T.J.S. and Menagh D.P., 1982, Evidence from Sr isotopes for long lived heterogenesis in the upper mantle. Nature, 298, 251~253.

Bender J.F., Langmuir C.H. and Hanson G.N., 1984, Petrogenesis of basalt glasses from the Tamayo region, East Pacific Rise. J. Petrol., 25, 213~254.

Ben Othman D., Polve M. and Allegre C.J., 1984, Nd-Sr isotopic composition of granulites and constraint on the evolution of the lower continental crust. Nature, 307, 510~515.

Bente K. and Nielsen H., 1982, Experimental S isotope fractionation studies between coexisting bismuthinite (Bi_2S_3) and sulphur (S_o). Earth Planet. Sci. Lett., 59, 18~20.

Bevins R.E., Kokelaar B.P. and Dunkley P.N., 1984, Petrology and geochemistry of lower to middle Ordovician igneous rocks in Wales: a volcanic arc to marginal basin transition. Proc. Geol. Ass., 95, 337~347.

Bhatia M.R., 1983, Plate tectonics and geochemical composition of sandstones. J. Geol., 91, 611~627.

Bhatia M.R. and Crook K.A.W., 1986, Trace element characteristics of graywacks and tectonic discrimination of sedimentary basins. Contrib. Mineral. Petrol., 92, 181~193.

Bickle M.J., Bettenay L.F., Chapman H.J., Groves D.I., McNaughton N.J., Campbell I.H. and de Laeter J.R., 1989, The age and origin of younger granitic plutons of the Shaw Batholith in the Archean Pilbara block, western Australia. Contrib. Mineral. Petrol., 101, 361~376.

Bjorlykke K., 1974, Geochemical and mineralogical influence of Ordovician island arcs on epicontinental clastic sedimentation. A study of lower Palaeozoic sedimentation in the Oslo region, Norway. Sedimentology, 21, 251~272.

Blanckenburg F.v., Villa I.M., Baur H., Morteani G. and Steiger R. H., 1989, Time calibration of a P-T-path from the Tauern window Eastern Alps: the problem of closure temperatures. Contrib. Mineral. Petrol., 101, 1~11

Blatt H., Middleton G. and Murray R., 1972, *Origin of sedimentary rocks. New Jersey*: Prentice Hall.

Bloomer S. and Stern R., 1990, Tectonic origins. Nature, 346, 518.

Bloxham W. and Lewis A.D., 1972, Ti, Zr, and Cr in some British pillow lavas and their petrogenetic affinities. Nature, 237, 134~136.

Bluth G.L. and Ohmoto H., 1988, Sulfide-sulfate chimneys on the East Pacific Rise, 11° and 13° N latitudes. Part II: Sulfur isotopes. Canad. Mineral., 26, 505~515.

Boles J.R. and Franks S.G., 1979, Clay diagenesis in Wilcox sandstones of southwest Texas: implications of smectite diagenesis on sandstone cementation. J. Sed. Petrol., 49, 55~70.

Boryta M. and Condie K.C., 1990, Geochemistry and origin of the Archaean Beit Bridge Complex, Limpopo Belt, South Africa. J. Geol. Soc. Lond., 147, 229~239.

Bottinga Y., 1969, Calculated fractionation factors between carbon and hydrogen isotope exchange in the system

calcite-carbon dioxide-graphite-methane-hydrogen-water vapour. Geochim. Cosmochim. Acta, 33, 49-64.

Bottinga Y. and Javoy M., 1973, Comments on oxygen isotope geothermometry. Earth Planet. Sci. Lett., 20, 250~265.

Bottinga Y. and Javoy M., 1975, Oxygen isotope partitioning among the minerals in igneous and metamorphic rocks. Rev. Space Phys. Geophys., 13, 401~418.

Bottinga Y. Weill D.F. and Richet P., 1981, Thermodynamic modelling of silicate melts. In Newton R.C., Navrotsky A. and Wood B. J. (eds.), Thermodynamics of minerals and melts. Advances in physical geochemistry series. Berlin: Springer, pp.207~245.

Bottrell S.H., Greenwood P.B., Yardley B.W.D., Sheppard T.J. and Spiro B., 1990, Metamorphic and post-metamorphic fluid floe in the low-grade rocks of the Harlech dome, north Wales. J. Metamorph. Geol., 8, 131~143.

Bougault H., Joron J.L., and Treuil M., 1980, The primordial chondritic nature and large-scale heterogeneities in the mantle: evidence from high and low partition coefficient elements in oceanic basalts. Phil. Trans. R. Soc. Lond., A297, 203~313.

Boynton W.V., 1984, Geochemistry of the rare earth elements: meteorite studies. In: Henderson P. (ed.), Rare earth element geochemistry.Elservier, pp. 63~114.

Brevart O., Dupre B. and Allegre C.J., 1986, Lead-lead age of komatiite lavas and limitations on the structure and evolution of the Precambrian mantle. Earth Planet. Sci. Lett., 77, 293~302.

Brewer T.S. and Atkin B.P., 1989, Element mobilities produced by low grade metamorphic events. A case study from the Proterozoic of southern Norway. Precamb. Res., 45, 143~158.

Brookins D.G., 1989, Aqueous geochemistry of rare earth elements. In: Lipin B.R. and McKay G.A. (eds). Geochemistry and mineralogy of rare earth elements, Rev. Mineral., 21, 201~225.

Brooks C., Hart S.R. and Wendt T., 1972, Realistic use of two-error regression treatments as applied to rubidium-strontium data. Rev. Geophys. Space Phys., 10, 551~577.

Brooks C.K., Henderson P. and Ronsbo J.G., 1981, Rare earth element partitioning between allanite and glass in the obsidian of Sandy Braes, northern Ireland. Mineral. Mag., 44, 157~160.

Brown G.C., Thorpe R.S. and Webb P.C., 1984, The geochemical characteristics of granitoids in contrasting arc and comments on magma sources. J. Geol. Soc. Lond., 141, 411~426.

Brugmann G.E., Arndt N.T., Hoffmann A.W. and Tobschall H.J., 1987, Nobel metal abundance in komatiite suites from Alexo, Ontario and Gorgona Island, Colombia. Geochim. Cosmochim. Acta, 51, 2159~2169.

Burcher-Nurminen K., 1981, The formation of metasomatic reaction veins in dolomitic marble roof pendants in the Bergell intrusion (Province Sondrio, northern Italy). Am. J. Sci., 281, 1197~1222.

Burrows D.R., Wood P.C. and Spooner E.T.C., 1986, Carbon isotope evidence a magmatic origin for Archean gold-quartz vein ore deposits. Nature, 321, 851~854.

Butler J.C., 1979, Trends in ternary petrological variation diagrams — fact or fantasy? Am. Mineral., 64, 1115~1121.

Butler J.C., 1981, Effect of various transformations on the analysis of percentage data. J. Math. Geol., 13, 53~68.

Butler J.C., 1982, Artificial isochrons. Lithos, 15, 207~214.

Butler J.C., 1986, The role of spurious correlation in the development of a komatiite alteration model. J. Geophys.

Res., 91, E275~280.

Butler J.C. and Woronow A., 1986, Discrimination among tectonic setting using trace element abundances of basalts. J. Geophys. Res., 91, B10289~B10300.

Cabanis B. and Lecolle M., 1989, Le diagramme La/10-Y/15-Nb/8: un outil pour la discrimination de series volcaniques et la mise en evidence des processus de melange et/ou de contamination crustale. C.R. Acad. Sci. Ser. II, 309, 2023~2029.

Cameron M. and Papike J.J., 1981, Structural and chemical variations in pyroxenes. Am. Mineral., 66, 1~50.

Campbell A.C. et al., 1988, Chemistry of hot springs on the Mid-Atlantic Ridge. Nature, 335, 514~519.

Campbell I.H., Naldrett A.J. and Barnes S.J., 1983, A model for the origin of the platinum-rich sulfide horizons in the Bushveld and Stillwater complexes. J. Petrol., 24, 133~165.

Carr P.E., 1985, Geochemistry of late Permian shoshonitic lavas from the southern Sydney Basin. In: Sutherland F.L., Franklin B.J. and Waltho A.E. (eds.), Volcanism in Eastern Australia. Geol. Soc. Aust., N.S.W., Div. Publ. No.1, pp.165~183.

Chaffey D. J., Cliff R.A. and Wilson B.M., 1989, Characterisation of the St Helena magma source. In: Saunders A.D. and Norry M.J. (eds.), Magmatism in ocean basins. Spec. Publ. Geol. Soc. No.42, pp.257~276.

Chamberlain C.P and Rumble D.,1988,Thermal anomalies in a regional metamorphic terrane: an isotopic study of fluids. J. Petrol.,29,1215~1232.

Chambers L. A., 1982, Sulfur isotope study of a modern intertidal environment and the interpretation of ancient sulfides. Geochim. Cosmochim. Acta, 46, 721~728.

Chaussidon M., Albarede F. and Sheppard S.M. F., 1989, Sulphur isotope variation in the mantle from ion microprobe analyses of micro-sulphide inclusion. Earth Planet. Sci. Lett., 92, 144~156.

Chaussidon M. and Lorand J.P., 1990, Sulphur isotope composition of orogenic spinel lherzolite massifs from Ariege (N.E. Pyrenees, France): An ion microprobe study. Geochim. Cosmochim. Acta, 54, 2835~2846.

Chayes F., 1949, On ratio correlation in petrography., J. Grol., 57, 239~254.

Chayes F., 1960, On correlation between variables of constant sum. J. Geophys. Res., 65, 4185~4193.

Chayes F., 1971, Ratio correlation Chicago Univ. Press.

Chayes F., 1977, Use of correlation statistics with rubidium-strontium systematics. Science, 196, 1234~1235.

Chayes F. and Velde D., 1965, On distinguishing between basaltic lavas of circumoceanic and ocean-island type by means of discriminant functions. Am. J. Sci., 263, 206~222.

Chiba H., Chachko T., Clayton R.N. and Goldsmith J.R., 1989, Oxygen isotope fractionation involving diopside, forsterite, magnetite and calcite: application to geothermometry. Geochim. Cosmochim. Acta, 53, 2985~2995.

Chivas A.R., Andrew A.S., Sinha A.K. and O'Neil J.R., 1982, Geochemistry of a Pliocene-Pleistocene oceanic-arc plutonic complex, Guadalcanal. Nature, 300, 139~143.

Chaisse F., 1989, Automated sample preparation for analysis of geological materials. In: Ahmedali S.T. (ed.), *X-ray fluorescence analysis in the geological sciences: Advances in Methodology*. Geol. Assn. Canada; Short course 7, pp.39~54.

Chaoue-Long J.C., Thirlwall M.F. and Nesbitt R., 1984, Sm-Nd systemmatics of Kambalda greenstones revisited and rivised. Nature, 307, 697~701.

Claypool G.E., Holser W.T., Kaplan I.R., Sakai H. and Zak I., 1980, The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. Chem. Geol., 28, 190~260.

Clayton R.N., 1981, Isotopic thermometry. In: Newton R.C., Navrotsky A. and Wood B.J. (eds.), *Thermodynamics of minerals and melts*. New York: Springer-Verlag, pp.85~109.

Clayton R.N., 1991, Oxygen isotope thermometer calibrations. In: Taylor H.P., O'Neil J.R., Kaplan I.R. (eds.), *Stable isotope geochemistry: a tribute to Samuel Epstein*, Geochemical Soc. Spec. Publ., No.3, 3~10.

Clayton R.N., O'Neil J.R. and Mayeda T.K., 1972, Oxygen isotope fractionation in quartz and water. J. Geophys. Res., 77, 3057~3067.

Clayton R.N., Goldsmith J.R. and Mayeda T.K., 1989, Oxygen isotope fractionation in quartz, albite, anorthite and calcite. Geochim. Cosmochim. Acta, 53, 725~733.

Cliff R.A., 1985, Isotopic dating in metamorphic belts. J. Geol. Soc. Lond., 142, 97~110.

Cliff R.A., Baker P.E. and Mateer N.J., 1991, Geochemistry of inaccessible island volcanics. Chem. Geol., 92, 251~260.

Cocherie A., Auge T. and Meyer G., 1989, Geochemistry of the platinum-group elements in various types of sponels from the Vourinos ophiolitic complex, Greece. Chem. Geol., 77, 27~39.

Cohen A.S., O'Nions R.K., Siegenthaler R. and Griffin W.L., 1988, Chronology of the pressure-temperature history recorded by a granulite terraine. Contrib. Mineral. Petrol., 98, 303~311.

Coleman M.L., 1977, Sulphur isotopes in petrology. J. Geol. Soc. Lond., 133, 593~608.

Coleman M.L. and Raisewell R., 1981, Carbon, oxygen and sulphur isotope variations in concretions from the Upper Lias of N.E. England. Geochim. Cosmochim. Acta, 45, 329~340.

Collerson K.D., Campbell L.M., Weaver B.L. and Palacz Z.A., 1991, Evidence for extreme mantle fractionation in early Archaen ultramafic rocks from northern Labrador. Nature, 349, 209~214.

Colson R.O., McKay G. A. and Taylor L.A., 1988, Temperature and composition dependencies of trace element partitioning: Olivine/melt and low Ca-pyroxene/melt. Geochim. Cosmochim. Acta, 52, 539~553.

Compston W., Williams I.S. and Meyer C., 1984, U-Pb geochronology of zircons from lunar breccia 73217 using a sensitive high mass-resolution ion microprobe. J. Geophys. Res., 89 (supplem.), B525~B534.

Condie K.C. and Crow C., 1990, Early Precambrian within-plate basalts from Kaapvaal craton in southern Africa: a case for comtaminated komatiites. J. Geol., 98, 100~107.

Condie K.C., Wilks M., Rosen D.M. and Zlobin V.L., 1991, Geochemistry of metasediments from the Precambrian Hapschan series, eastern Anabar Shield, Siberia. Precamb. Res., 50, 37~47.

Condie K.C. and Wronkiewicz D.S., 1990, The Ce/Th ratio in Precambrian pelites from the Kaapvaal Craton as an index of cratanic evolution. Earth Planet. Sci. Lett., 97, 256~267.

Connolly C. and Muehlenbachs K., 1988, Contrasting oxygen diffusion in nepheline, diopside and other silicates and their relevance to isotopic systematics in meteorites. Geochim. Cosmochim. Acta,, 52, 1585~1591.

Coplen T.B., Kendall C. and Hopple J., 1983, Comparison of stable isotope reference standars. Nature, 302, 236~238.

Coryell C.G., Chase J.W. and Winchester J.W., 1963, A procedure for geochemical interpretation of terrestrial rare-earth abundance patterns. J. Geophys. Res., 68, 559~566.

Cox K.G., Bell J.D. and Pankhurst R.J., 1979, *The interpretation of igneous rocks.London:* Allen and Unwin.

Cox K. G. and Clifford P., 1982, Correlation coefficient patterns and their interpretation in three basaltic suites. Contrib. Mineral. Petrol., 79, 268~278.

Cross W., Iddings J.P., Pirsson L.V. and Washington H.S., 1903, *Quantitative classification of igneous rocks*. Univ. Chicago Press.

Cullers R.L., 1988. Mineralogical and chemical changes of soil and stream sediment formed by intense weathering of the Danburg granite, Geogia, U.S.A. Lithos, 21, 301~314.

Cullers R.L., Barrett T., Carlson R. and Robinson B., 1987, Rare-earth element and mineralogic changes in Holocene soil and stream sediment: a case study in the Wet Mountains, Colorado, U.S.A. Chem. Geol., 63, 275~297.

Cullers R.L., Basu A. and Suttner L.J., 1988, Geochemical signature of provenance in sand-mixed material in soils and stream sediments near the Tobacco Root Batholith, Montana, U.S.A. Chem. Geol., 70, 335~348.

Cumming G.L. and Richards J.R., 1975, Ore lead isotope ratios in a continuously changing earth. Earth Planet Sci. Lett., 28, 155~171.

Date A.R. and Jarvis K.E., 1989, The applications of ICP-MS in the earth sciences. In: Date A.R. and Gray A L. (eds.), *The applications of inductively coupled plasma mass spectrometry*. Glasgow: Blackie, pp. 43~70.

Davidson J.P., 1983, Lesser Antilles isotopic evidence of the role of subducted sediment in island arc magma genesis. Nature, 306, 253~256.

Davies G.R., Gledhill A. and Hakesworth C., 1985, Upper crustal recycling in southern Britain: evidence from Nd and Sr isotopes. Earth Planet. Sci. Lett., 75, 1~12.

Deines P. and Gold D.P., 1973, The isotopic composition of carbonatite and kimberlite carbonates and their bearing on the isotopic composition of deep seated carbon. Geochim. Cosmochim. Acta, 37, 1709~1733.

Deines P., 1989, Stable isotope variations in carbonatites. In Carbonatites: genesis and evolution, Bell K.(ed.). London: Unwin Hyman, 301~359.

De la Roche H., Leterrier J., Grande Claude P and Marchal M., 1980, A classification of volcanic and plutonic rocks using R1-R2 diagrams and major element analyses — its relationship and current nomenclature. Chem Geol., 29, 183~210.

Deloule E., Albarede F. and Sheppard S.M.F., 1991, Hydrogen isotope heterogeneities in the mantle from ion probe analyses of amphiboles from ultramafic rocks. Earth Planet. Sci. Lett., 105, 543~553.

DePaolo D.J., 1981a, Neodymium isotopes in the Clorado Frant range and crust-mantle evolution in the Proterozoic. Nature, 291, 193~196.

DePaolo D.J., 1981b, Trace element and isotopic effects of combined wallrock assimilation and fractional crystallisation. Earth Planet. Sci. Lett. , 53, 189~202.

DePaolo D.J., 1982, Sm-Nd, Rb-Sr and U-Th-Pb systematics of granulite facies rocks from Fyfe Hills, Enderby Land, Antarctica. Nature, 298, 614~618.

DePaolo D.J., 1988, *Neodymium isotope geochemistry: an introduction*. New York: Springer Verlag.

DePaolo D.J. and Wasserburg G.J., 1976, Nd isotopic variations and petrogenetic models. Geophys. Res Lett., 3, 249~252.

DePaolo D.J. and Wasserburg G.J., 1979, Petrogenetic mixing models and Nd-Sr isotopic patterns. *Geochim.*

Cosmochim. Acta, 43, 615~627.

Dickin A.P., 1987, La-Ce dating of Lewisian granulites to constrain the ^{138}La β-decay half life. Nature, 325, 337~338.

Dickson J A.D., 1991, Disequilibrium carbon and oxygen isotope variations in natural calcite Nature, 353, 842~844

Dodson M.H., 1973, Closure temperature in cooling geochronilogical and petrological systems. Contrib. Mineral Petrol , 40, 259~274.

Dodson M.H., 1979, Theory of cooling ages. In: Jager E. and Hunziker J.C. (eds.), *Lectures in isotope geology.* New York: Springer-Verlag, pp.194~202.

Dodson M.H., 1982, On 'spurious' correlations Rb-Sr isochron diagrams. Lithos, 15, 215~219.

Doe B.R. and Zartman R.E., 1979, Plumbotectonics. In: Barnes H. (ed.), *Geochemistry of hydrothermal ore deposit.* Chapter 2. New York: Wiley.

Dostal J., Dupuy C., Carron J.P., Le Guen de Kerneizon M. and Maury R. C., 1983, Partition coefficients of trace elements: application to volcanic rocks of St Vincent, West Indies. Geochim. Cosmochim. Acta, 47, 525~533.

Downes H. and Dupuy C., 1987. Textural, isotopic and REE variations in spinel peridotite xenoliths, Massif central, France. Earth Planet. Sci. Lett., 82, 121~135.

Downes H. and Leyreloup A., 1986, Granulitic xenoliths from the French Massif Central — petrology, Sr and Nd isotope systematics and model age estimates. In: Dawson J.B., Carswell D.A., Hall J. and Wedepohl K.H.(eds.), *The nature of the lower crust.* Geol. Soc. Lond. Spec. Publ. 24, pp.319~330.

Drake M.J. and Holloway J. R., 1981, Partitioning of Ni between olivine and silicate melt: the 'Henry's Law problem' reexamined. Geochim. Cosmochim. Acta, 45, 431~437.

Drake M.J. and Weill D.F., 1975, Partition of Sr, Ba, Ca, Y, Eu^{2+}, Eu^{3+} and other REE between plagioclase felspar and magmatic liquid: an experimental study. Geochim. Cosmochim. Acta, 39, 689~712.

Draper N.R. and Smith H., 1981, *Applied regression analysis.* 2nd edition. New York: Wiley.

Duncan A.R., 1987, The Karoo igneous province — a problem area for inferring tectonic setting frm basalt geochemistry. J. Volc. Geothermal Res., 32, 13~34.

Dunn T., 1987, Partitioning of Hf, Lu, Ti and Mn between olivine, clinopyroxene and basaltic liquid Contrib. Mineral. Petrol., 96, 476~484.

Eissen J-P , Juteau T., Joron J-L., Dupre B., Humler E. and Al'Mukhamedov A., 1989, Petrology and geochemistry of basalts from the Red Sea axial rift at 18 deg north. J. Petrol., 30, 791~839.

Elderfield H., 1986, Strontium isotope stratigraphy. Palaeogeogr. Palaeoclimatol. Palaeoecol., 57, 71~90

Elderfield H., 1988, The oceanic chemistry of the rare-earth elements. Phil. Trans. R. Soc. Lond., A325, 105~126.

Elderfield H. and Greaves M.J., 1981, Negative cerium anomalies in the rare earth element patterns of oceanic ferromanganese nodules. Earth Planet. Sci. Lett., 55, 163~170.

Elderfield H. and Greaves M.J., 1982, The rare earth elements in seawater. Nature, 296, 214~219.

Eldridge C.S., Compston W., Williams I.S., Both R.A., Walshe J.L. and Ohmoto H., 1988, Sulfur isotope variability in sediment-hosted massive sulfide deposits as determined using the ion-microprobe, SHRIMP: I. An example from the Rammelsberg ore body. Econ. Geol., 83, 443~449.

Ellam R.M. and Hawkesworth C.J., 1988, Elemental and isotopic variations in subduction related basalts: evidence for a three component model. Contrib. Mineral. Petrol., 98, 72~80.

Elthon D., 1983, Isomolar and isostructural pseodo-liquidus phase diagrams for oceanic basalts. Am. Mineral , 68, 506~511.

England J-O. and Jorgensen P., 1973, A chemical classification system for argillaceous sediments and factors affecting their composition. Geol. Foren. Stockholm Foeh., 95, 87~97.

Epstein S., 1970, Antarctic ice sheet: stable isotope analysis of Byrd Station coves and interhemispheric climatic implications. Science, 168, 570~572.

Epstein S., Buchsbaum R., Lowenstam H.A. and Urey H.C , 1953, Revised carbonate-water isotopic temperature scale. Geol. Soc. Am. Bull., 64, 1315~1326.

Epstein S., Sharp R.P. and Gow A.J, 1965, Six-year record of hydrogen and oxygen isotope variations in South Pole fur. J. Geophys. Res., 70, 1809~1814.

Ernst R.E., Fowler A.D. and Pearce T. H., 1988, Modelling of igneous fractionation and other processes using Pearce diagrams. Contrib. Mineral. Petrol., 100, 12.

Eugster H.P. and Wones D.R., 1962, Stability relations of ferromagnesian biotite, annite. J. Petrol., 3, 82~125.

Evensen N.M., Hamilton P.J. and O'Nions R.K., 1978, Rare earth abundances in chondritic meterorites. Geochim. Cosmochim. Acta, 42, 1199~1212.

Ewart A., 1982, The mineralogy and petrology of Tertiary-Recent orogenic volcanic rocks with special reference to the andisitic-basaltic composition range. In: Thorpe R.S.(ed.), Andesites. Chichester: Wiley, pp.25~87

Exley R.A., Mattey D.P., Clague D.A. and Phillinger C.T., 1986, Carbon isotope systematics of a mantle 'hot-spot': a comparison of Loihi seamount anf MORB glasses. Earth Planet. Sci. Lett., 78, 189~199.

Farver J.R., 1989, Oxygen self diffusion in diopside with application to cooling rate determination. Earth Planet. Sci. Lett., 92, 386~396.

Faure G., 1977, Principles of isotope geology. New York: Wiley.

Faure G., 1986, Principles of isotope geology. 2nd edition, New York: Wiley.

Faure G., Hoefs J. and Mensing T.M., 1984, Effect of oxygen fugacity on sulphur isotope compositions and magnetite concentrations in the Kirkpatrick basalt, Mount Falla, Queen Alexanda Range, Antarctica. Isotope Geosci., 2, 301~311.

Fears D., 1985, A corrected CIPW norm program for interactive use. Computer Geosci., 11, 787~797.

Ferry J.M., 1983, Mineral reactions and element migration during metamorphism of calcareous sediments from the Vasselboro Formation, south-cental Maine. Am. Mineral., 68, 334~354.

Field C.W. and Fifarek R.H., 1986, light stable isotope systematics in the epithermal environment. In: Berger B.R. and Bethke P.M. (eds.), Geology and geovhemistry of epithermal systems. Society of Economic Geologists. Rev. Econ. Geol., 2, 99~128.

Fitton J.G., James D., Kempton P.D., Ormerod D.S. and Leeman W.P., 1988, The role of the lithospheric mantle in the generation of late Cenozoic basix magmas in the western United States. J. Petrol., Special Lithosphere issue, 331~349.

Fleet A.R., 1984, Aqueous and sedimentary geochemistry of the rare earth elements. In: *Henderson P. (ed.), Rare*

Earth Element Geochemistry, Elsevier, pp.331~373.

Flegal A.R., Itoh K., Patterson C.C. and Wong C.S., 1986, Vertical profile of lead isotopic compositions in the north-east Pacific. Nature, 321, 689~690.

Fletcher I.R. and Rosman K.J.R., 1982, Precise determination of initial ε_{Nd} from Sm-Nd isochron data. Geochim. Cosmochim. Acta, 46, 1983~1987.

Fletcher T.A., Boyce A.J. and Fallick A.E., 1989, A sulphur isotope study of Ni-Cu mineralisation in the Huntly-Knock Caledonian mafic and ultramafic intrusions of northeast Scotland. J. Geol. Soc. Lond., 146, 675~684.

Floyd P.A. and Winchester J.A., 1975, Magma-type and tectonic setting discrimination using immobile elements. Earth Planet. Sci Lett., 27, 211~218.

Floyd P.A., Winchester J.A. and Park R.G., 1989, Geochemistry and tectonic setting of Lewisian clasic metasediments from the early Proterozoic Loch Maree group of Gairloch, NW Scotland. Precamb. Res., 45, 203~214.

Francis D., 1985, The pyroxene paradox in MORB glasses — A signature of picritic parental magmas? Nature, 319, 586~589.

Friedman I. and O'Neil J.R., 1977, *Data of geochemistry*. Compilation of stable isotope fractionation factors of geochemical interest. U.S. G.S. Professional Paper. 440~kk.

Fujimaki H., 1986, Partition coefficients of Hf, Zr and REE between zircon, apatite and liquid. Contrib. Mineral Petrol., 94, 42~45.

Fujimaki H., Tatsumoto M. and Aoki K., 1984, Partition coefficients of Hf, Zr and REE between phenocrysts and groundmasses. Proceedings of the fourteenth lunar and planetary science conference, Part 2. J. Geophys. Res., 89, Supplm. B662~B667.

Galer S.J.G. and O'Nions R.K., 1985, Residence time of thorium, uranium and lead in the mantle with implication for mantle convection. Nature, 316, 778~782.

Garcia M O., 1978, Criteria for the identification of ancient volcanic areas. Earth Sci. Rev., 14, 147~165

Garcia R.B. and Frias J.M., 1990, BITERCLA: GW-basic program to plot classification diagrams. Computer Geosci., 16, 265~271.

Gebauer D. and Grunenfelder M., 1979, U-Th-Pb dating of minerals. In: Jaguar E. and Hunker J.C. (eds.), *Lectures in isotope geology*. New York: Springer-Verlag, pp.105~131.

Gelnas L., Mellinger M. and Trudel P., 1982, Archaean mafic metavolcanics from the Rouyn-Noranda district, Abitibi greenstone belt, Quebec. 1. Mobility of the major elements. Can. J. Earth Sci., 19, 2258~2275.

Gerlach D.C, Cliff R.A, Davies G.R., Norry M.J. and Hodgson N., 1988, Magmasources of the Cape Verdes archipelago: isotopic and trace element constraints. Geochim. Cosmochim. Acta, 52, 2979~2992.

Ghiorso M.S., 1985, Chemical mass transfer in magmatic processes. I. Thermodynamic relations and numerical algorithms. Contrib. Mineral. Petrol., 90, 107~120.

Ghiorso M.S. and Carmichael I.S.E., 1985, Chemical mass transfer in magmatic processes. II. Application inequilibrium crystallsation, fractionation and assimilation. Contrib. Mineral. Petrol., 90, 107~121~141.

Giletti B.J., 1986, Diffusion effects on oxygen isotope temperatures of slowly cooled igneous and metamorphic rocks. Earth Planet. Sci. Lett., 77, 218~228.

Gill J.B., 1981, Orogenic andisites and plate tectonics. Berlin: Springer.

Girard J-P., Savin S.M . and Aronson J.L., 1989, Diagenesis of the lower Cretaceous arkoses of the Angola margin: petrologic, K/Ar dating and $^{18}O/^{16}O$ evidence. J. Sed. Petrol., 59, 519~538.

Glazer A.F , 1984, A short CIPW norm. Computer Geosci., 10, 449~450.

Goldstein S.L., O'Nions R.K. and Hamilton P.J., 1984, A Sm-Nd study of atmospheric dusts and particulates from major river systems . Earth Planet. Sci. Lett., 70, 221~236.

Gonfiantini R., 1978, Standards for stable isotope measurements in natural compounds. Nature, 271, 534~536.

Govindaraju K., 1984, 1984 compilation of working values and sample description for 170 international reference samples of mainly silicate rocks and minerals. Geostandards Newsletter, Special Issue no.8.

Graham C.M. and Harmon R.S., 1983, Stable isotope evidence on the nature of crust-manlte interactions. In: Hawkesworth C.J. and Norry M.J. (eds.), Continental basalts and mantle xenoliths. Nantwich: Shva, pp.20~45.

Graham C.M., Harmon R.S. and Sheppard S.M.F., 1984, Experimental hydrogen isotope studies: hydrogen isotope exchange between amphibole and water. Am. Mineral., 69, 128~138.

Graham C.M., Sheppard S.M.F. and Heaton T.H.E., 1980, Experimental hydrogen isotope studies I: Systematics of hydrogen isotope fractionation in the systems epidote-H_2O, zoisite- H_2O and AlO(OH)- H_2O. Geochim. Cosmochim. Acta., 44, 353~364.

Gray C..M., Cliff R.A. and Goode AD.T., 1981, Neodymium-strontium isotopic evidence for extreme comtamination in a layered basic intrusion. Earth Planet. Sci. Lett., 56, 189~198.

Green T.H. and Pearson N.J., 1985a, Experimental determination of REE partition coefficients between amphibole and basaltic liquids at high pressure. Geochim. Cosmochim. Acta, 49, 1465~1468.

Green T.H. and Pearson N.J., 1985b, Rare earth element partitioning between clinopyroxene and silicate liquid at moderate to high pressure. Contrib. Mineral. Petrol., 91, 24~36.

Green T.H. and Pearson N.J., 1986, Rare-earth element partitioning between sphene and coexisting silicate liquid at high pressure and temperature. Chem. Geol., 55, 105~119.

Green T.H. and Pearson N.J., 1987, An experimental study of Nb and Ta partitioning between Ti-rich minerals and silicate liquids at high pressure and temperature. Geochim. Cosmochim. Acta, 51, 55~62.

Green T.H., Sie S.H., Ryan C.G. and Cousens D.R., 1989, Proton microprobe-determined partitioning of Nb, Ta, Zr, Sr and Y between garnet, clinopyroxene and basaltic magma at high pressure and temperature. Chem Geol., 74, 201~216.

Gregory R.T. and Taylor H.P., 1981, An oxygen isotope profile in a section of Cretaceous oceanic crust, Semail ophiolite Oman: evidence for $\delta^{18}O$ buffering of the oceans by deep (>5 km) seawater — hydrothermal circulation at mid-ocean ridges. J. Geophys. Res., 86, 2737~2755.

Gregory R.T., Criss R.E. and Taylor H.P., 1989 Oxygen isotope exchange kinetics of mineral pairs in close and open systems: application to problems of hydrothermal alteration of igneous rocks and Precambrian iron formations. Chem. Geol., 75, 1~42.

Gromet L.P., Dymek R.F., Haskin L.A. and Korotev R.L., 1984, The "North American Shale Composite": its compilation, major and trace element characteristics. Geochim. Cosmochim. Acta, 48, 2469~2482.

Grove T.L., Gerlach D.C. and Sando T.W., 1982, Origin of late calc-alkaline series lavas at Medicine Lake Volcano by fractionation, assimilation and mixing. Contrib. Mineral. Petrol., 80, 160~182.

Grove T.L., Gerlach D.C. and Sando T.W., 1983, Origin of late calc-alkaline series lavas at Medicine Lake Volcano by fractionation, assimilation and mixing: corrections and clarifications. Contrib. Mineral. Petrol., 82, 407~408.

Groves D.I., Golding S.D., Rock N.M.S., Barley M.E. and McNaughton N.J., 1988, Archean carbon reservoirs and their relenace to the fluid soure for gold deposits. Nature, 331, 254~257.

Hagen H. and Neumann E-R., 1990, Modelling of trace element distribution in magma chambers using open system models. Computer Geosci., 16, 549~586.

Halbach P. et al., 1989, Probable modern analogue of Kuroko-type massive sulphide deposits in the Okinawa Trpugh back-arc basin. Nature, 338, 496~499.

Hall A., 1987, Igneous Petrology. London: Longman.

Hamilton D.L. and MacKenzie W.S., 1965, Phase equilibria studies in the system $NaAlSiO_4$(nepheline)-$KAlSiO_4$(kalsilite)-SiO_2-H_2O. Mineral. Mag., 34, 214~231.

Hamilton P.J., Evensen N.M., O'Nions R.K. and Tarney J., 1979a, Sm-Nd systematics of Lewsian gneisses implications for the origin of granulites. Nature, 277, 25~28.

Hamilton P.J., Evensen N.M., O'Nions R.K. , Smith H.S. and Erlank A.J., 1979b, Sm-Nd dating of Onverwacht group volcanics, southern africa. Nature, 279, 298~300.

Hanson G.N., The application of trace elements on the petrogenesis of igneous rocks of granitic composition. Earth Planet. Sci. Lett., 1978, 38, 26~43.

Hanson G.N. and Langmuir C.H., 1978, Modelling of major and trace elements in mantle-melt systems using trace element approaches. Geochim. Cosmochim. Acta, 42, 725~741.

Harker A., 1909, *The natural history of igneous rocks.* London: Methuen.

Harmer R.E. and Eglington B.M., 1987, The mathematics of geochronometry: Equations for use in regression calculations. National Physical Research Laboratory, Geochronology Division C.S.I.R., South Africa.

Harris N.B.W., Pearce J.A. and Tindle A.G., 1986, Geochemical characteristics of collision-zone magmatism. In: Coward M.P. and Reis A.C. (eds.), *Collision tectonics.* Spec. Publ. Grol. Soc. Lond., 19, 67~81.

Harris P.G., 1974, Origin of alkaline magmas as a result of anatexis. In: Sorenson H. (ed.), The alkaline rocks. London: John Wiley & Sons.

Harrison A.G. and Thode H.G., 1957, The kinetic isotope effect in the chemical reduction of sulphate. Trans. Faraday Soc., 53, 1648~1651.

Harrison T.M. and McDougall I., 1980, Investigation of an intrusive contact in NW Nelson, New Zealand. I. Thermal, chronological and isotopic constraints. Geochim. Cosmochim. Acta, 44, 1985~2003.

Hart M.B. and Leary P.N., 1989, The stratigraphic and palaeogeographic setting of the late Cenomanian 'anoxic' event. J. Geol. Soc. Lond., 146, 305~310.

Hart S.R., 1984, A large-scale isotope anomaly in the the southern hemisohere mantle. Nature, 309, 753~757.

Hart S.R. and Davis K.E., 1978, Nickel partitioning between olivine and silicate melt. Earth Planet. Sci. Lett., 40, 203~219.

Haskin L.A., Haskin M.A., Frey F.A. and Wildman T.R., 1968, Relative and absolute terrestrial abundances of the rare earths. In: Ahrens L.H. (ed.), Origin and distribution of the elements, vol.1. Oxford: Pergamon, pp.889~

911.

Haskin M.A. and Frey F.A., 1966, Dispersed and not-so-rare earths. Science, 152, 299~314.

Haskin M A. and Haskin L.A., Rare earths in European shales: a redetermination. Science, 154, 507~509.

Hattori K., 1989, Barite-celestine intergrowths in Archean plutons: the product of oxidising hydrothermal activity related to alkaline intrusions. Am. Mineral., 74, 1270~1277.

Hattori K., Campbell F.A. and Krouse H.R., 1983, Sulphur isotope abundances in Aphebian clastic rocks: implications for the coeval atmosphere. Nature, 302, 323~326.

Haughton P.D.W., 1988, Acryptic Caledonian flysch terrane in Scotland. J. Geol. Soc. Lond., 145, 685~703

Hawkesworth C.J., Hammill M., Gledhill A.R., van Calsteren P.W.C. and Rogers G., 1982, Isotope and trace element evidence for late-stage intra-crustal melting in the High Andes. Earth Planet. Sci. Lett., 58, 240~254.

Hawkesworth C.J., Marsh J.S., Duncan A.R., Erlank A.J. and Norry M.J., 1984, The role of continental lithosphere In the generation of the Karoo volcanic rocks: evidence from combined Nd- and Sr-isotope studies. Spec. Publ. Geol. Soc. S. Africa, 13, 341~354.

Hawkesworth C.J. and van Calsteren P.W.C., 1984, Radiogenic isotopes — some geological applications. In: Henderson P. (ed.), *Rare earth element geochemistry*. Amsterdam: Elsevier, pp.375~421.

Helz R.T., 1987, Diverse olivene types in lava in the 1959 eruption of Kilauea volcano and their bearing on eruption dynamics. In: Decker R.W., Wright T.L. and Stauffer P.H., (eds.), *Volcanism in Hawaii* USGS Prof. Paper 1350, pp.691~722.

Henderson P., 1982, Inorganic geochemistry. Oxford: Pergamon.

Henderson P. and Pankhurst R.J., 1984, Analytical chemistry. In: Henderson P. (ed.), *Rare earth element geochemistry*. Amsterdam: Elsevier, pp. 467~499.

Hergt J..M., Chappell B.W., McCulloch M.T., McDougall I. and Chivas A.R., 1989, Geochemical and isotopic constraints on the origin of Jurassic dolerites of Tasmania. J. Petrol., 30, 841~883.

Herron M..M., 1988, Geochemical classification of terrigenous sands and shales from core or log data. J. Sed. Petrol., 58, 820~829.

Herron M..M. and Herron S.L., 1990, Geological applications of geochemical well logging. In: Hurst A., Lovell M.A. and Morton A.C. (eds.), *Geological application of wireline logs*, Sepc. Publ. Geol. Soc. Lond., No.48, pp.165~175.

Hertogen J. and Gijbels R., 1976, Calculation of trace element fractionation during partial melting. Geochim. Cosmochim. Acta, 40, 313~322.

Herzberg C.T., 1992, Depth and degree of melting of komatiites. J. Geophys. Res., 97, 4521~4540.

Hickson C.J. and Juras S.J., 1986, Sample contamination and grinding. Canad. Mineral., 24, 585~589.

Hildreth W., 1981, Gradients in silicic magma chambers: implications for lithospheric magmatism. J. Geophys. Res., 86, B10153~B10192.

Hinton R.W., 1990, Ion microprobe trace-element analysis of silicates: measurement of multi-element glasses. Chem. Geol., 83, 11~25.

Hirt B., Tilton G.R., Herr W. and Hoffmeister W., 1963, The half-life of ^{187}Re. In: Geiss J. and Goldberg E.D.(eds.), Earth science and meteorites. Amsterdam: North Holland, pp.273~280.

Hoefs J., 1987, *Stable isotpe geochemistry*. 3rd edition, Berlin: Springer-Verlag.

Hoernle K., Tilton G. and Schmincke H-U., 1991, Sr-Nd-Pb isotopic evolution of Gran Canaria: evidence for shallow enriched mantle beneath the Canary Islands. Earth Planet. Sci. Lett., 106, 44~63.

Hoffman A., Gruszczynski M. and Malkowski K., 1991, On the interrelationship between temporal trends in $\delta^{13}C$, $\delta^{18}O$ and $\delta^{34}S$ in the world ocean. J. Geol., 99, 355~370.

Hoffmann A.W. and Hart S.R., 1978, An assessment of local and regional isotopic equilibrium in the mantle. Earth Planet. Sci. Lett., 38, 44~62.

Holm P.E., 1982, Non-recognition of continental tholeiites using the Ti-Y-Zr diagram. Contrib. Mineral. Petrol., 79, 308~310.

Holm P.E., 1990, Complex petrogenetic modelling using spreadsheet software. Computer Geosci., 16, 1117~1122.

Hooker P.J., Hamilton P.J. and O'Nions R.K., 1981, An estimate of the Nd isotpic composition of iapetus seawater from ca 490 Ma metalliferous sediments. Earth Planet. Sci. Lett., 56, 180~188.

Hostetler C.J. and Drake M.J., 1980, Predicting major element mineral/melt equilibria: a statistical approach. J. Geophys.Res., 85, 3789~3796.

Hoyle J., Elderfield H., Gledhill A. and Greaves M., 1984, The behaviour of the rare-earth elements during the mixing of river and sea waters. Geochim. Cosmochim. Acta, 48, 143~149.

Huang W~L. and Wyllie P.J., 1975, Melting relations in the system $NaAlSi_3O_8$-KAl Si_3O_8-SiO_2 to 35 kilobars, Dry and excess water. J. Geol., 83, 737~748.

Hudson J.D., 1977, Stable isotopes and limestone lithification. J. Geol. Soc. Lond., 133, 637~660.

Huebner M., Kyser T.K. and Nisbet E.G., 1986, Stable-isotope geochemisrty of the high-grade metapelites from the central zone of the Limpopo belt. Am. Mineral., 71, 1343~1353.

Humphries S.E., 1984, The mobility of the rare earth elements in the crust. In: Henderson P. (ed.), *Rare earth element geochemistry*. Amsterdam: Elsevier, pp.315341.

Innocenti F., Manetti P., Mazzuuoli R., Pasquare G. and Villari, 1982, Anatolia and north-western Iran. In: Thorpe R.S. (ed.), Andisites. Chichester: Wiley, pp.327~349.

Irvine T.N. and Baragar W.R.A., 1971, A guide to the chemical classification of the common volcanic rocks. Canad. J. Earth Sci., 8, 523~548.

Irvine A.J., 1978, A review of experimental studies of crystal/liquid trace element partitioning. Geochim. Cosmochim. Acta, 42, 743~770.

Irvine A.J. and Frey F.A., 1978, Distribution of trace elements between garnet megacrysts and host volcanic liquids of kimberlitic to rhyolitic composition. Geochim. Cosmochim. Acta, 42, 771~787.

Jackson D.H., Mattey D.P. and Harris N.B.W., 1988, Carbon isotope compositions of fluid inclusions in charnockites from southern India. Nature, 333, 167~170.

Jacobsen S.B. and Wasserburg G.J., 1980, Sm-Nd isotopic evolution of chondrites. Earth Planet. Sci. Lett., 50, 139~155.

Jager E. and Hunziker J.C. (eds), 1977, *Lectures in isotope geology*. New York: Springer-Verlag.

Jagoutz E., Palme H. et al., 1979, The abundances of major, minor and trace elements in the earth's mantle as derived from primitive ultramafic nodules. Proc. Lunar and Planet. Sci. Conf. No.10, Geochim. Cosmochim.

Acta, Supplement 11, 2031~2050.

Jahn B.-M., Vidal P. and Tilton G.R., 1980, Arcgaean mantle heterogeneity: evidence from chemical and isotopic abundances in Archaean igneous rocks. Phil. Trans. R., Soc. Lond., A297, 354~364.

James D.E., 1981, The combined use of oxygen and radiogenic isotopes as indicators of crustal contamination. Ann. Rev. Earth Planet. Sci., 9, 311~344.

James R.S. and Hamilton D.L., 1969, Phase relations in the system $NaAlSi_3O_8$-$KAlSi_3O_8$-$CaAl_2$ Si_2O_8-SiO_2 at 1 kilobar water vapour pressure. contrib. Mineral. Petrol., 21, 111~141.

Jarvis K.E. and Williams J.G., 1989, The analysis of geological samples by slurry nebulisation inductively coupled plasma-mass spectrometry (ICP-MS). Chem. Geol., 77, 53~63.

Javoy M., 1977, Stable isotopes and geothermoetry. J Geol. Soc. Lond., 133, 609~636.

Javoy M., Fourcade S. and Allegre C.J., 1970, Graphical method for examining $^{18}O/^{16}O$ fractionation in silicate rocks. Earth Plant. Sci. Lett., 10, 12~16.

Javoy M., Pineau F. and Ilyama I., 1978, Experimental determination of the isotopic fractionation between gaseous CO_2 and carbon dessolved in tholeiitic magma: a preliminary study. Contrib. Mineral. Petrol., 67, 35~39.

Jenkin G.R.T., Fallick A.E., Farrow C.M. and Browes G.E., 1991, COOL: a FORTRAN-77 computer program for modelling stable isotopes in cooling closed systems. Computer Geosci., 17, 391~412.

Jenner G.J., Lonerich H.P., Jackson S.E. and Fryer B.J., 1990, ICP-MS a powerful tool for high presision trace-element analysis in earth sciences; evidence from analysis of selected U.S.G.S. reference samples. Chem. Geol., 83, 133~148.

Jensen L.S., 1976, A new cation plot for classifying subalkalic volcanic rocks. Ontario Div. Mines. Misc. Pap. 66.

Jensen L.S. and Pyke D.R., 1982, Komatiites in the Ontario portion of the Abitibi belt. In: Arndt N.T. and Nisbet E.G. (eds.), Komatiites. London: George Allen and Unwin, pp.147~157.

Jochum K.P., Seufert H.M. and Thirwall M.F., 1990, High-sensitivity Nb analysis by spark source mass spectrometry (SSMS) and calibration of XRF Nb and Zr. Chem. Geol., 81, 1~16.

Johnannes W., 1980, Metastable melting in granite system Qz-Or-Ab-An-H_2O. Contrib. Mineral. Petrol., 72, 73~80.

Johnannes W., 1983, Metastable melting in granite and related systems. In: Atherton M.P. and Gribble C.D. (eds), Migmatites, melting and metamorphism. Shiva, pp.27~36.

Johnannes W., 1984, Beginning of melting in the granite system Qz-Or-Ab-An- H_2O. Contrib. Mineral. Petrol., 86, 264~273.

Kay R.W. and Hubbard N.J., 1978, Trace elements in ocean ridge basalts. Earth Planet. Sci. Lett., 38, 95~116.

Kelley S.P. and Fallick A.E., 1990, High precision spatially resolved analysis of $\delta^{34}S$ in sulphides using a laser extraction technique. Geochim. Cosmochim. Acta, 54. 883~888.

Kelsey C.H., 1965, Calculation of the CIPW norm. Mineral. Mag., 34, 276~282.

Kenny B.C., 1982, Beware spurious self-correlation in allometry. Biometrika, 37, 30~41.

Krrich R. and Fryer B.J., 1979, Archaean preciuos-metal hydrothermal systems, Dome Mine, Abitibi greenstone belt. II, REE and oxygen isotope relations. Canad. J. Earth Sci., 16, 440~458.

Kerridge J.F., 1985, Carbon, hydrogen and nitrogen in carbonaceous chondrites: abundances and isotopic

compositions in bulk samples. Geochim. Cosmochim. Acta, 49, 1707~1714.

Kilinc A., Carmichael I.S.E., Rivers M.L. and Sack R.O., 1983, The ferric-ferrous ratio of natural silicate liquids equilibrated in air. Contrib. Mineral Petrol., 83, 136~140.

Kramers J.D., Smith C.B., Lock N.P., Harmon R.S. and Boyd F.R., 1981. Can Kimberlites be generated from ordinary mantle? Nature, 291, 53~56.

Kreulen R., 1988, High integrated fluid-rock ratios during metamorphism a Naxos: evidence from carbon isotopes of calcite in schists and fluid inclusions. Contrib. Mineral. Petrol., 98, 28~32.

Kronberg B.L., Murray F.H., Daddar R. and Brown J.R., 1988, Fingerprinting geological materials using SMSS. Chem. Geol., 68, 351~359.

Kroner A., Williams I.S., Compston W., Baur N., Vitanage P.W. and Perera L.R.K., 1987, Zircon ion microprobe dating of high-grade rocks in Sri Lanka. J. Geol., 95, 775~791.

Kuno H., 1966, Lateral variation of basalt magma types across continental margins and island arcs Bull. Volcanol., 29, 195~222.

Kuno H., 1968, Differentiation of basalt magmas. In: Hess H.H. and Poldervaart A. (eds.), Basalts: The Poldervaart treatise on rocks of basaltic composition, Vol.2, New York: Interscience, pp.623~688.

Kyser T.K. and O'Neil J.R., 1984, Hydrogen isotope systematics of submarine basalts. Geochim. Cosmochim.Acta, 48, 2123~2133.

Kyser T.K., O'Neil J.R. and Carmichael I.S.E., 1981, Oxygen isotope thermometry of basic lavas and mantle nodules. Contrib. Mineral. Petrol., 77, 11~23.

Kyser T.K., O'Neil J.R. and Carmichael I.S.E., 1982, Genetic relations among basic lavas and ultramafic nodules: evidence from oxygen isotope compositions. Contrib. Mineral. Petrol., 81, 88~102.

Land L.S. and Dutton S.P., 1978, Cementation of a Pennylvanian deltaic sandstone: isotopic data. J. Sed. Petrol., 48, 1167~1176.

Langmuir C.H., 1989, Geochemical consequences of in situ crystallisation. Nature, 340, 199~205.

Langmuir C.H., Bender J.F., Bence A.E., Hanson G.N. and Taylor S.R., 1977, Petrogenesis of basalts from the FAMOUS area: mid-Atlantic ridge. Earth Planet. Sci. Lett., 36, 133~156.

Langmuir C.H. and Hanson G.N., 1980, An evaluation of major element heterogeneity in the mantle sources of basalts. Phil. Trans. R. Soc. Lond., A297, 383~407.

Langmuir C.H., Vocke R.D., Hanson G.N. and Hart S.R., 1978, A general mixing equation with applications to icelandic basalts. Earth Plant. Sci. Lett., 37, 380~392.

Leake B.E., Hendry G.L. et al., 1969, The chemical analysis of rock powers by automated X-ray fluorescence. Chem. Geol., 5, 7~86.

Lechler P.J. and Desilets M.O., 1987, A review of the use of loss on ignition as a measurement of total volatiles in whole rock analysis. Chem. Geol., 63, 341~344.

Leeman W.P. and Lindstrom D.J., 1978, Partitioning of Ni^{2+} between basaltic melt and synthetic melts and olivines – an experimental study. Geochim. Cosmochim. Acta, 42, 801~816.

Le Maitre R.W., 1968, Chemical variation within and between volcanic rock series– a statistical approach. J.

Petrol., 9, 220~252.

Le Maitre R.W., 1976, The chemical variability of some common igneous rocks. J. Petrol., 17, 589~637.

Le Maitre R.W., 1981, GENMIX — a generalised petrological mixing model program. Computer Geosci., 7, 229~247.

Le Maitre R.W., Bateman P., Dudek A., Keller J., Lameyre J., Le Bas M.J., Sabine P.A., Schmid R., Sorensen H., Streckeisen A., Wooley A.R. and Zanettin B., 1989, A Classification of igneous rocks and glossary of terms. Oxford: Blackwell.

Leterrier J., Maury R.C., Thonon P., Girard D. and Marchal M., 1982, Clinopyroxene composition as a method of identification of the magmatic affinities of palaeo-volcanic series. Earth Planet. Sci. Lett., 59, 139~154.

Liew T.C. and McCulloch M.T., 1985, Genesis of granitoid batholiths of Penisular Malaysia and implications for models of crustal evolution ; Evidence from a Nd-Sr isotopic and U-Pb lead study. Geochim. Cosmochim. Acta, 49, 587~600.

Lindstrom D.J. and Weill D.F., 1978, Partitioning of transition metals between diopside and coexisting silicate liquids. I. Nickel, cobalt and manganese. Geochim. Cosmochim. Acta, 42, 817~831.

Long J.V.P., 1967, Electron probe microanalysis. In: Zussman J. (ed.), Physcal methods in determinative mineralogy. New York: Academic Press.

Long P.E., 1978, Experimental determination of partition coefficients for Rb, Sr and Ba between alkali feldspar and silicate liquid. Geochim. Cosmochim. Acta, 42, 833~846.

Lugmair G.W. and Marti K., 1978, Lunar initial $^{143}Nd/^{144}Nd$: differential evolution of the lunar crust and mantle. Earth Planet. Sci. Lett., 39, 349~357.

Lugmair G.W. , Scheinin N.B. and Marti K., 1975, Search for extinct ^{146}Sm, 1. The isotopic abundance of ^{142}Nd in the Juvinas meteorite. Earth Planet. Sci. Lett., 27, 79~84.

Luth W.C., 1969, The systems $NaAlSi_3O_8$-SiO_2 and $KAlSi_3O_8$-SiO_2 to 20 kb and the relationship between H_2O content, P_{H2O} and P_{total} in granitic magmas. Am. J. Sci., 267A, 325~341.

Luth W.C., Jahns R.H. and Tuttle O.F., 1964, The granite system at pressures of 4~10 kbars. J. Geophys. Res., 69, 759~773.

Maas R. and McCulloch M.T., 1991, The provenance of Archaean clastic metasediments in the Narryer Gneiss Complex, western Australia: trace element geochemistry, Nd isotopes and U-Pb ages for detrital zircons. Geochim. Cosmochim. Acta, 55, 1915~1932.

McConnaughey T., 1989, ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates: I. Patterns. Geochim. Cosmochim. Acta, 53, 53, 151~162.

McCulloch M.T. and Black L.P., 1984, Sm-Nb isotpic systematics of Enderby Land granulites and evidence for the redirtribution of Sm and Nd during metamorphism. Earth Planet. Sci. Lett., 71, 51~64.

McCulloch M.T. and Chappell B.W., 1982, Nd isotopic characteristics of S- and I-type granites. Earth Planet. Sci. Lett., 58, 51~64.

McCulloch M.T., Jaques A.L., Nelson D.R. and Lewis J.D., 1983, Nd and Sr isotopes in kimberlites and lamproites from western Australia: an enriched mantle origin. Nature, 302, 400~403.

McDermott F. and Hawkesworth C.J., 1991, Th, Pb and Sr isotopic variations in young island arc volcanics and

oceanic sediments. Earth Planet. Sci Lett., 104, 1~15.

MacDonald G.A., 1968, Composition and origin of Hawaiian lavas. In: Coats R.R., Hay R.L. and Anderson C.A. (eds.), *Studies in volcanology*: a memoir in honour of Howel Williams. Geol. Soc. Am. Mem. 116, 477~522.

MacDonald G.A. and Katsura T., 1964, Chemical composition of Hawaiian lavas. J. Petrol., 5, 83~133.

McDonough W.F., Sun S.-S., Ringwood A.E., Jagoutz E. and Hoffmann A.W., 1991, K, Rb and Cs in the earth and moon and the evolution of the earth's mantle. Geochim. Cosmochim. Acta, Ross Taylor Symposium volume.

MacGeehan P.J. and MacLean W.H., 1980, An Archaean sub-seafloor geothermal system, 'calc-alkali' trends, and massive sulphide genesis. Nature, 286, 767~771.

McIntire W.L., 1963, Trace element partition coefficients — a review of theory and applications to geology. Geochim. Cosmochim. Acta, 27, 1209~1264.

McKenzie D., 1985, The extraction of magma from the crust and mantle. Earth Planet. Sci. Lett., 74, 81~91.

McLennan S.M, 1989, Rare earth elements in sedimentary rocks: influence of provenance and sedimentary processes. In: Lipin B.R and McKay G.A. (eds.), Geochemistry and mineralogy of rare earth elements. Rev. Mineral., 21, pp.169~200.

McLennan S.M and Taylor S.R., 1991, Sedimentary rocks and crustal evolution revisited: tectonic setting and secular trends. J. Geol., 99, 1~21.

McLennan S.M , Taylor S.R., McCulloch M.T. and Maynard J.B., 1990, Geochemical and Nd-Sr isotopic composition of deep sea turbidites: crustal evolution and plate tectonic associations. Geochim. Cosmochim. Acta, 54, 2015~2050.

Magaritz M., Whitford D.J. and James D.E., 1978, Oxygen isotopes and the origin of high $^{87}Sr/^{86}Sr$ andesites. Earth Planet. Sci. Lett., 40, 220~230.

Mahood G. and Hidreth W., 1983, Large partition coefficients for trace elements in high-silica rhyolites. Geochim. Cosmochim. Acta, 47, 11~30.

Manning D.A.C., 1981, The effect of fluorine on liquidus phase relationships in the system Oz-Ab-Or with excess water at 1 kb. Contrib. Mineral. Petrol., 76, 206~215.

Marshall B.D. and DePaolo D.J., 1982, Precise age determinations and petrogenetic studies using the K-Ca method. Geochim. Cosmochim. Acta, 46, 2537~2545.

Marumo K., Nagasawa K. and Kuroda Y., 1980, Mineralogy and hydrogen isotope chemistry of clay minerals in the Ohunuma grothermal area, NE Japan. Earth Planet. Sci. Lett., 47, 255~262.

Mason B. (ed.)., 1971, *Handbook of elemental abundances in meteorites.* New York: Gordon and Breach.

Masuda A., 1962, Regularities in variation of relative abundances of lanthanide elements and an attempt to analyse separation-index patterns of some minerals. J. Earth Sci. Nagoya Univ., 10, 173~187.

Masuda A., Nakamura N. and Tanaka T., 1973, Fine structures of mutually normalised rare-earth patterns of chondrites. Geochim. Cosmochim. Acta, 37, 239~248.

Matsuhisa Y., Goldsmith J.R. and Clayton R.N., 1979, oxygen isotope fractionation in the systems quartz-albite-anorthite-water. Geochim. Cosmochim. Acta, 43, 1131~1140.

Matsui A., Onuma N., Nagasawa H., Higuchi H. and Banno S., 1977, Crystal structure control in trace element partition between crystal and magma. Bull. Soc. Fr. Mineral. Crysllogr., 100, 315~324.

Matthews A., Goldsmith J.R. and Clayton R.N., 1983, Oxygen isotope fractionation involving pyroxenes: the calibration of mineral-pair thermometers. Geochim. Cosmochim. Acta, 47, 631~644.

Matthews A. and Katz A., 1977, Oxygen isotope fractionation during the dolomitisation of calcium carbonate. Geochim. Cosmochim. Acta, 41, 1431~1438.

Mauche R., Faure G., Jones L.M. and Joefs J., 1989, Anomalous isotopic compositions of Sr, Ar and O in the mesozoic diabase dykes of Liberia, West Africa. Contrib. Mineral. Petrol., 101, 12~18.

Mearns E.W., Knarud R., Raestad N, Stanley K.O. and Stockbridge C.P, 1989, Samarium-neodymium isotope stratigraphy of the Lunde and Statfjord formations of Snorre oil field, northern North Sea. J. Geol. Soc. Lond., 146, 217~228.

Meisch A.T., 1969, The constant sum problem in geochemistry. In: Merriam D.F. (ed.), Computer applications in the earth sciences. New York: Plenum Press, pp.161~176.

Mensing T.M., Faure G., Jones L.M., Bowman J.R. and Hoefs J., 1984, Petrogenesis of the Kirkpatrick basalt, Solo Nunatak, northern Victoria Land Antarctica, based upon isotopic compositions of strontium, oxygen and sulfur. Contrib. Mineral. Petrol., 87, 101~108.

Menzies M.A. and Halliday A., 1988, Lithospheric domains beneath the Archaean and Proterozoic crust of Scotland. J. Petrol., Special Lithosphere Issue, 275~302.

Merlet C. and Bodinier J.-L., 1990, Electron microprobe determination of minor and trace transition metal elements in silicate minerals: a method and its application to mineral zoning in the peridotite nodule PHN 1611. Chem. Geol., 83, 55~69.

Merrill R.B., Robertson J.K. and Wyllie P.J., 1970, Melting reactions in the system $NaAlSi_3O_8$-K $AlSi_3O_8$-SiO_2-H_2O to 20 kilobars compared with results for other feldspar-quratz-H_2O and rock- H_2O systems. J. Geol., 78, 558~569.

Meschede M., 1986, A method of discriminating between different types of mid-ocean ridge basalts and continental tholeiites with the Nb-Zr-Y diagram. Chem. Geol., 56, 207~218.

Michael P.J., 1988, Partition coeffecients for rare earth elements in mafic minerals of high silica rhyolites: the importance of accessory mineral inclusions. Geochim. Cosmochim. Acta, 52, 275~282.

Michard A., Gurriet P, Soudant M. and Albarede F., 1985, Nd isotope in French phanerozoic shales: external vs internal aspects of crustal evolution. Geochim. Cosmochim. Acta, 49, 601~610.

Michard A., 1989, Rare earth element systematics in hydrothermal fluids. Geochim. Cosmochim. Acta, 53, 745~750.

Middlemost E.A.K., 1975, The basalt clan. Earth Sci. Rev., 11, 337~364.

Middlemost E.A.K., 1985, *Magma and magmatic rocks*. London: Longman.

Middlemost E.A.K., 1989, Iron oxidation ratios, norms and the classification of volcanic rocks. Chem. Geol., 77, 19~26.

Middleton G.V., 1960, Chemical composition of sandstones. Bull. Geol. Soc. Am., 71, 109~126.

Miller K.G. and Fairbanks R.G., 1985, Ceinozoic $\delta^{18}O$ record of climate and sea level. S. Afr. J. Sci., 81, 248~249.

Miller K.G. and O'Nions R.K., 1985, Source of Precambrian chemical and clasic sediments. Nature, 314, 325~330

Minster J.F. and Allegre C.J., 1978, Systematic use of trace elements in igneous processes. Part III: Inverse problem of batch partial melting in volcanic suites. Contrib. Mineral. Petrol., 68, 37~52.

Minster J.F., Minster J.B., Treuil M and Allegre C.J., 1977, Systematic use of Systematic use of trace elements in igneous processes. Part II: Inverse problem of the fractional crystallization process in volcanic suites. Contrib. Mineral. Petrol., 61, 49~77.

Miyoshi T., Sakai H. and Chiba H., 1984, Experimental study of sulphur isotope fractionation factors between sulphate and sulphide in high temperature melts. Geochem. J., 18, 75~84.

Moorbath S., Powell J.L. and Taylor P.N., 1975, Isotopic evidence for the age and origin of the "grey gneiss" complex of the southern Outer Hebrides, Scotland. J. Geol. Soc. Lond., 131, 213~222.

Moran P.A.P., 1971, Estimating structural and functional relationships. J. Multivariate Anal., 1, 232~255.

Morrison G.W., 1980, Characteristics and tectonic setting of the shoshonite rock association. Lithos, 13, 97~108.

Morrison M.A., 1978, The use of "immobile" trace elements to distinguish the palaeotectonic affinities of metabasalts: applications to the palaeocene basalts of Mull and Skye, northwest Scotland. Earth Planet. Sci. Lett., 39, 407~416.

Morse S.A., 1969, Syenites Carn. Inst. Wash. YBK, 67, 112~120.

Morse S.A., 1970, Alkali feldspars with water at 5kb pressure. J. Petrol., 11, 221~253.

Mottl M.J., 1983, Metabasalts, axial hot springs, and the structure of hydrothermal systems at mid-ocean ridges. Geol. Soc. Am. Bull., 94, 161~180.

Muecke G.K., 1980, *Neutron activation analysis in the geoscience. Mineral Assoc. Canada short course handbook 5.*

Muehlenbachs K. and Byerly G., 1982, ^{18}O-enrichment of silicic magmas caused by crystal fractionation at the Galapagos spreading center. Contrib. Mineral. Petrol., 79, 76~79.

Muehlenbachs K. and Clayton R.N., 1976, Oxygen isotope composition of oceanic crust and its bearing on sea water. J. Geophys. Res., 81, 4365~4369.

Muenow D.W., Garcia M.O., Aggrey K.E., Bednarz U. and Schmincke H.U., 1990, Volatiles in submarine glasses as a discriminant of tectonic origin: application to the Troodos ophiolite. Nature, 343, 159~161.

Musasa S.B. and Henry D.S., 1990, The San Nicolas batholith of coastal Peru: early Palaeozoic continental arc or continental rift magmatism? J. Geol. Soc. Lond., 147, 27~39.

Mullen E.D., 1983, $MnO/TiO_2/P_2O_5$: a minor element discriminant for basaltic rocks of oceanic environments and its implications for petrogenesis. Earth Planet. Sci. Lett., 62, 53~63.

Nabelek P.I., Labotka T.C., O'Neil J.R. and Papike J.J., 1984, Contrasting fluid/rock interaction between Notch peak granite intrusion and argillites and limestones in western Utah: evidence from stable isotopes and phase assemblages. Contrib. Mineral. Petrol., 86, 25~34.

Nakai S., Shimizu H. and Masuda A., 1986, A new gechronometer using lanthanum-138. Nature, 320, 433~435.

Nakamura N., 1974, Determination of REE, Ba, Fe, Mg, Na, and K in carbonaceous and ordinary chondrites. Geochim. Cosmochim. Acta, 38, 757~775.

Naldrett A.J. and Duke J.M., 1980, Platinum metals in magmatic sulfide ores. Science, 208, 1417~1427.

Naldrett A.J., Hoffman E.L., Green A.H., Chou C-L., Naldrett S.R. and Alcock R.A, 1979, The composition of Ni-sulfide ores with particular reference to their content of PGE and Au. Canad. Mineral., 17, 403~415.

Nash W.P. and Crecraft H.R., 1985, Partition coefficients for trace elements in silicic magmas. Geochim Cosmochim. Acta., 49, 2309~2322.

Nathan H.D. and Van Kirk C.K., 1978, A model of magmatic crystallisation. J. Petrol., 19, 66~94.

Naylor H.,, Turner P., Vaughan D.J., Boyce A.J. and Fallick A.E., 1989, Gentic studies of redbed mineralisation in the Triassic of the Cheshire basin, northwest England. J. Geol. Soc. Lond., 146, 685~699.

Neilsen R.L., 1988, A model for the simulation of combined major and trace element liquid lines of descent. Geochim, Cosmochim. Acta,52, 27~38.

Nelson B.K. and DePaolo D.J., 1984, 1700 Myr greenstone volcanic successions in southwestern North America and isotopic evolution of Proterozoic mantle. Nature, 312, 143~146.

Nesbitt H.W., 1979, Mobility and fractionation of rare earth elements during weathering of a granodiorite. Nature, 279, 206~210.

Nesbitt H.W., MacRae N.D. and Kronberg B.I., 1990, Amazon deep-sea fan muds: light REE enriched products of exteme chemical weathering. Earth Planet. Sci. Lett., 100, 118~123.

Nesbitt H.W. and Young G.M., 1982, Early Proterozoic climates and plate motions infered from major element chemistry of lutites. Nature, 299, 715~717.

Nesbitt H.W. and Young G.M., 1984, Prediction of some weathering trends of plutonic and volcanic rocks based unpon thermodynamic and kinetic considerations. Geochim. Cosmochim. Acta, 48, 1523~1534.

Nesbitt H.W. and Young G.M., 1989, Formation and diagenesis of weathering profiles. J. Geol., 97, 129~147.

Nicholls J., 1988, The statistcs of Pearce element diagrams and the Chayes closue problem. Contrib. Mineral. Petrol., 99, 11~24.

Nisbet E.G. et al., 1987, Uniquely fresh 2.7 Ga komatiites from the Belingwe greenstone belt, Zmbabwe. Geology, 15, 1147~1150.

Nisbet E.G., Deitrich V.J. and Esenwein A., 1979, Routine trace element determination in silicate minerals and rocks by X-ray fluorescence. Forschr. Miner., 57, 264~279.

Nisbet E.G. and Pearce J.A., 1977, Clinopyroxene composition in mafic lavas from different tectonic settings Contrib. Mineral. Petrol., 63, 149~160.

Norman M.D. and De Deckker P., 1990, Trace metals in lacustrine and marine sediments: a case study from the gulf of Carpentaria, northern Australia. Chem. Geol., 82, 299~318.

Norman M.D. and Leeman W.P., 1990, Open-system magmatic evolution of andesites and basalts from the Salmon Creek volcanics, southwest Idaho, U.S.A. Chem. Geol., 81, 167~189.

Norrish K. and Chappell B.W., 1967, X-ray fluorescence spetrography. In: Zussman J. (ed.), Physical methods in determinative mineralogy. New York: Academic Press, pp.161~214.

Norrish K. and Chappell B.W., 1977, X-ray fluorescence spetrography. In: Zussman J. (ed.), Physical methods in determinative mineralogy, 2nd edition. New York: Academic Press, pp.201~272.

Norrish K. and Hutton J.T., 1969, An accurate X-ray spectrographic method for the analysis of a wide range of geological samples. Geochim. Cosmochim. Acta, 33, 431~453.

O'Connor J.T., 1965, A classification for quartz-rich igneous rock based feldspar ratios. USGS Prof. Paper 525B, B79~B~84.

O'Hara M.J., 1965, The bearing of phase equilibria studies on the origin and evolution of basic and ultrabasic rocks. Earth Sci. Rev., 4, 69~133.

O'Hara M.J., 1977, Geochemical evolution during fractional crystallization of a periodically refilled magma chamber. Nature, 266, 503~507.

O'Hara M.J., 1980, Nonliner nature of the unavoidable long-lived isotopic, trace and major element contamination of a developing magma chamber. Phil. Trans. R. Soc., 297, 215~227.

O'Hara M.J. and Mattews R.E., 1981, Geochemical evolution in an advancing, periodically replenished, periodically tapped, continuously fractionated magma chamber. J. Geol. Soc. Lond., 138, 237~277.

Ohmoto H., 1986, Stable isotope geochemistry of ore deposits. In: Valley J.W., Taylor H.P. and O'Neil J.R. (eds.), *Stable isotopes and high temperature geological processes*. Rev. Mineral., 16, pp.460~491.

Ohmoto H. and Lasaga A.C., 1982, Kinetics of reactions between aqueous sulphates and sulphides in hydrothermal systems. Geochim. Cosmochim. Acta, 46, 1727~1745.

Ohmoto H. and Rye R.O., 1974, Hydrogen and oxygen isotopic compositions of fluid inclusions in the Kuroko deposits, Japan. Econ. Geol., 69, 947~953.

Ohmoto H. and Rye R.O., 1979, Isotopes of sulfur and carbon. In: Barnes H.L. (ed.), Geochemistry of hydrothermal ore deposits. New York: Wiley, 509~567.

O'Neil J.R., Clayton R.N. and Mayeda T.K., 1969, Oxygen isotope fractionation in divalent metal carbonates. J. Chem. Phys., 51, 5547~5558.

O'Neil J.R. and Taylor H.P., 1967, The oxygen isotope and cation exchange chemistry of feldspars. Am. Mineral., 52, 1414~1437.

O'Nions R.K., Carter S.R., Evensen N.M. and Hamilton P.J., 1979, Chemical and cosmochemical applications of Nd isotope analysis. Ann. Rev. Earth Planet. Sci., 7, 11~38.

O'Nions R.K., Hamilton P.J. and Evensen N.M., 1977, Variations in $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ in oceanic basalts. Earth Planet. Sci. Lett., 34, 13~22.

O'Nions R.K., Hamilton P.J. and Hooker P.J., 1983, A Nd isotope investigation of sediments related to crustal development in the British Isles. Earth Planet. Sci. Lett., 63, 229~240.

O'Nions R.K. and McKenzie D.P., 1988, Melting and continent generation. Earth Planet. Sci. Lett., 90, 449~456.

Onuma N., Clayton R.N. and Mayeda T.K., 1972, Oxygen isotope cosmothermometer. Geochim. Cosmochim. Acta, 36, 169~188.

Onuma N., Higuchi H., Wakita H. and Nagasawa H., 1968, Trace element partitioning between two pyroxenes and the host lava. Earth Planet. Sci. Lett., 5, 47~51.

Oskarsson N., Sigvaldson G.E. and Steinthorsson S., 1982, A dynamic model of rift zone petrogenesis and the regional petrology of Iceland. J. Petrol., 23, 28~74.

Patchett P.J. and Tasumoto M., 1980, Lu-Hf total-rock isochron for eucrite meteorites. Nature, 288, 571-574.

Pearce J.A., 1976, Statistical analysis of major element patterns in basalts. J. Petrol., 17, 15~43.

Pearce J.A., 1980, Geochemical evidence for the genesis and eruptive setting of lavas from Tethyan ophiolites. Proc. Int. Ophiolite Symp., Cyprus 1979. Institute of Mining and Metallurgy, pp.261~272.

Pearce J.A., 1982, Trace element characteristics of lavas from destructive plate boundaries. In: Thorpe R.S. (ed.),

Andesits. Chichester: Wiley, pp. 525~548.

Pearce J.A., 1983, Role of the sub-continental lithosphere in magma genesis at active continental margins. In: Hawkesworth C.J. and Norry M.J. (eds.), Continental basalts and mantle xenoliths. Nantwich : Shiva, pp.230~249.

Pearce J.A., 1987, An expert system for tectonic characterisation of ancient volcanic rocks. J. Volc. Geothermal Res., 32, 51~65.

Pearce J.A., Alabaster T., Shelton A.W. and Searle M.P., 1981, The Oman ophiolite as a Cretaceous arc-basin complex: evidence and implications. Phil. Trans. R. Soc. A300, 299~300.

Pearce J.A. and Cann J.R., 1971, Ophiolite origin investigated by discriminant analysis using Ti, Zr and Y. Earth Planet. Sci. Lett., 12, 339~349.

Pearce J.A. and Cann J.R., 1973, Tectonic setting of basic volcanic rocks determined using trace element analysis. Earth Planet Sci. Lett., 19, 290~300.

Pearce J.A. and Gale G.H., 1977, Identification of ore-deposition environment from trace element geochemistry of associated igneous host rocks. Geol. Soc. Spec. Publ., 7, 14~24.

Pearce J.A., Harris N.B.W. and Tindle A.G., 1984, Trace element discrimination diagrams for the tectonic interpretation of granitic rocks. J. Petrol, 25, 956~983.

Pearce J.A. and Norry M.J., 1979, Petrogenetic implications of Ti, Zr, Y and Nb variations in volcanic rocks. Contrib. Mineral. Petrol., 69, 33~47.

Pearce T.H., 1968, A contribution to the theory of variation diagrams. Contrib. Mineral. Petrol., 19, 142~157.

Pearce T.H., 1970, Chemical variations in the Palisades Sill. J. Petrol., 11, 15~32.

Pearce T.H., Gorman B.E. and Birkett T.C., 1975, The TiO_2-K_2O-P_2O_5 diagram: a method of discriminatinf between oceanic and non-oceanic basalts. Earth Planet. Sci. Lett., 24, 419~426.

Pearce T.H., Gorman B.E. and Birkett T.C., 1977, The relationship between major element chemistry and tectonic environment of basic and intermediate volcanic rocks. Earth Planet. Sci. Lett., 36, 121~132.

Peccerillo R. and Taylor S.R., 1976, Geochemistry of Eocene calc-alkaline volcanic rocks from the Kastamonu area, northern Turkey. Contrib. Mineral. Petrol, 58, 63~81.

Perfit M.R., Gust D.A., Bence A.E., Arculus R.J. and Taylor S.R., 1980, Chemical characteristics of island arc basalts: implications for mantle sources. Chem. Geol., 30, 227~256.

Peterson D.W. and Moore R.B., 1987, Geologic history and evolution of geologic concepts, Island of Hawaii. In: Decker R.W., Wright T.L. and Stauffer P.H. (eds.), *Volcanism in Hawaii*. USGS Prof. Paper 1350, Vol.1, pp.149~189.

Pttijohn F.J., Potter P.E. and Siever R., 1972, Sand and sandstones. New York: Springer-Verlag.

Peucat J.J., Vidal P., Bernard-Griffiths J. and Condie K.C., 1988, Sr, Nd and Pb isotopic systematics in the Archaean low- to high-grade transition zone of southern India: syn accretion vs. post-accretion granulites. J Geol., 97, 537~550.

Philpotts J.A., 1978, The law of constant rejection. Geochim. Cosmochim. Acta, 42, 909~920.

Philpotts J.A. and Schnetzler C.C., 1970, Phenocryst-matrix partition coefficients for K, Rb, Sr and Ba with applications to anorthosite and basalt genesis. Geochim. Cosmochim. Acta, 34, 307~322.

Piccirillo E.M., Civetta L., Petrini R. et al., 1989, Regional variations within the Parana flood basalt basalts

(southern Brazil): evidence for subcontinental mantle heterogeneiyt and crustal contamination. Chem. Geol., 75, 103~122.

Potter P.E., 1978, Petrology and chemistry of modern big river sands. J, Geol., 86, 423~449.

Potter P.E., Shimp N.F. and Witters J., 1963, Trace elements in marine and fresh-water argillaceous sediments. Geochim. Cosmochim. Acta, 27, 669~694.

Potts P.J., Webb P.C. and Watson J.S., 1990, Exploiting energy dispersive X-ray fluorescence spetrometry for the determination of trace elements in geological samples. Anal. Proc., 27, 67~70.

Powell R., 1984, Inversion of the assimilation and fractional crysllisation (AFC) equations; characterisation of contaminants from isotope and trace lement relationships in volcanic suites. J. Geol. Soc. Lond., 141, 447~452.

Presnall D.C. and Hoover J.D.,1984, Composition and depth of origin of primary mid-ocean ridge basalts. Contrib. Mineral. Petrol., 87, 170~178.

Presnall D.C., Dixon J.R., O'Donnell T.H. and Dixon S.A., 1979, Generation of mid-ocean ridge tholeiites. J.Petrol., 20, 3~35.

Prestvick T., 1982, Basic volcanic rocks and tectonic setting. A discussion of the Zr-Ti-Y discrimination diagram and its suitability for classification purposes. Lithos, 15, 241~247.

Price W.J., 1972, *Analytical atomic absorption spetrometry*. London: Heyden.

Rautenschlein M., Jenner G.A., Hertogen J., and Hofmann A.W. et al., 1985, Isotopic and trace element composition of volcanic glasses from the Akaki Canyon, Cyprus: implications for the origin of the Troodos ophiolie. Earth Planet. Sci. Lett., 75, 369~383.

Reed S.J.B., 1989, Ion microprobe analysis —a review of geological applications. Mineral. Mag., 53, 3~24.

Reuter A. and Dallmeyer R.D., 1989, K-Ar and $^{40}Ar/^{39}Ar$ dating of cleavage formed during very low grade metamorphism: a review. Daly J.S., Cliff R.A. and Yardley B.W.D. (eds.), *Evolution of metamorphic belts*, Spec. Publ. Geol. Soc. Lond. 43, 161~172.

Richardson C.K., Rye R.O. and Wasserman M.D., 1988, The chemical and thermal evolution of the fluids in the Cave-in-rock fluospar district, Illinois: stable isotope systematics at the Deardorff mine. Econ. Geol., 83, 765~783.

Richardson S.H., Gurney J.J., Erlank A.J. and Harris J.W., 1984, Origin of diamonds in old enriched mantle. Nature, 310, 198~202.

Richter D.H. and Moore J.G., 1966, Petrology of the Kilauea Iki lava lake, Hawaii. USGS Prof. Paper 537~B, B1~B26.

Richter F.M., 1986, Simple models for trace element fractionation during melt segregation. Earth Planet. Sci. Lett., 77, 333~344.

Rickwood P.C., 1989, Boundary lines within petrologic diagrams which use oxides of major and minor elements. Lithos, 22, 247~263.

Robinson P., Higgins N.C. and Jenner J.G., 1986, Determination of rare earth elements, yttrium and scandium in rocks by an ion-exchange X-ray fluorescence technique. Chem. Geol., 55, 121~137.

Rock N.M.S., 1987a, ROBUST: An interactive FORTRAN-77 package for exploratory data analysis using

parametric robust and nonparametric location and scale estimates, data transformations, normality tests and outlier assessment. Computer Geosci., 13, 463~494.

Rock N.M.S., 1987b, The need for standardization of normalised multi-element diagrams in geochemistry: a comment. Geochem. J., 21, 75~84.

Rock N.M.S., 1988a, *Numerical geology: a source guid, glossary and selective bibliography to geological uses of computers and statistics.* Springer-Verlag lecture notes in earth sciences, vol. 18.

Rock N.M.S., 1988b, Summary statistics in geochemistry: a study of the performance of robust estimates. Math. Geol., 20, 243~275.

Rock N.M.S., 1989, Reply to Aitchison . Math. Geol., 21, 791~793.

Roeder P.L. and Emslie R.F., 1970, Olivine-liquid equilibrium. Contrib. Mineral. Petrol., 29, 275~289.

Roelandts I., 1988, Comparison of inductively coupled plasma and neutron activation analysis for precise and accurate determination of nine rare-earth elements in geological materials. Chem. Geol., 67, 171~180.

Rogers N.W. and Hawkesworth C.J., 1982, Proterozoic age and cumulate origin foe granulitic xenoliths, Lesotho. Nature, 299, 409~413.

Rollinson H.R., 1983, The geochemisrty of mafic and ultramafic rocks from the Archaean greenstone belts of Sierra Leone. Mineral. Mag., 47, 267~280.

Rollinson H.R., 1992, Another look at the constant sum problem in geochemistry. Mineral. Mag., 56, 469~475.

Rollinson H.R. and Roberts C.R., 1986, Ratio correlation and major element mobility in altered basalts and komatiites. Contrib. Mineral. Petrol., 93, 89.

Roser B.P. and Korsch R.J., 1986, Determination of tectonic setting of sandstone-mudstone suites using SiO_2 content and K_2O/Na_2O ratio. J. Geol., 94, 635~650.

Roser B.P. and Korsch R.J., 1988, Provenance signatures of sandstone-mudstone suites determined using discriminan function analysis of major-element data. Chem. Geol., 67, 119~139.

Rumble D. III and Hoering T.C., 1986, Carbon isotope geochemistry of graphic vein deposits from New Hampshire USA. Geochim. Cosmochim. Acta, 50, 1239~1247.

Rumble D. III and Spear F.S., 1983, Oxygen isotope equilibration and permeability enhancement during regional metamorphism. J. Geol. Soc. Lond., 140, 619~628.

Russell J.K., Nicholls J., Stanley C.R. and Pearce T.H., 1990, Pearce element ratios. a paradigm for testing hypotheses. Eos, 71, 234~247.

Rutherford E. and Soddy F., 1903, Radioactive change. Phil. Mag., 6, 576~591.

Rye R.O. and Ohmoto H., 1974, Sulfur and carbon isotopes and ore genesis. A review. Econ. Geol., 69, 826~842.

Rye R.O., Schuiling R.D., Rye D.M. and Jansen J.B.H., 1976, Carbon hydrogen and oxygen isotope studies of the regional metamorphic complex at Naxos, Green. Geochim Cosmochim. Acta, 40, 1031~1049.

Ryerson F.J. and Hess P.C., 1978, Implications of liquid-liquid distribution coefficients to mineral-liquid partitioning. Geochim Cosmochim. Acta, 42, 921~932.

Schs L., 1984, *Applied statistics: a handbook of techniques, 2nd edition.* New York: Springer-Verlag.

Sack R.O., Charmichael I.S.E., Rivers M. and Ghiorso M.S., 1980, Ferri-ferrous equilibria in natural silicate liquids at 1 bar. Contrib. Mineral. Petrol., 75, 369~376.

Sakai H., Casadevall T.J. and Moore J.G., 1982, Chemistry and isotope ratios of sulfur in basalts and volcanic gases at Kilauea volcano, Hawaii. Geochim Cosmochim. Acta, 46, 729~738.

Sakai H., Des Maris D.J., Ueda A. and Moore J.G., 1984, Concentrations and isotope ratios of carbon, nitrogen and sulfur in ocean-floor basalts and volcanic gases at Kilauea volcano, Hawaii. Geochim Cosmochim. Acta, 48, 2433~2441.

Sangster D F., 1968, Relative sulfur isotope abundance of ancient seas and stratabound sulfide deposits. Proc. Geol. Assoc. Canada, 19, 79~86.

Saunders A.D., Norry M.J. and Tarney J., 1988, Origin of MORB and chemically depleted mantle reservoirs: trace element constraints. J. Petrol., Special Lithosphere Issue, 425~445.

Saunders A.D. and Tarney J., 1984, Geochemical characteritics of basaltic volcanism within back-acr basins. In: Kokelaar B.P. and Howells M.F. (eds.), *Marginal basin geology*, Spec. Publ. Geol. Soc. London 16, pp 59~76.

Savin S.M. and Lee M., 1988, Isotopic study of phyllosilicates. In: Bailey S.W. (ed.), *Hydrous phyllosilciate (exclusive of muscovite)*.Rev. Mineral., 19, pp.189~223.

Schairer J.F., 1950, The Alkali feldspar join in the system NaAl Si_3O_8-K Al Si_3O_8-SiO_2. J. Geol., 58, 512-517.

Schairer J.F. and Bowen N.L., 1935, Preliminary report on equilibrium relations between feldspathoids, alkali feldspars and silca. Trans. Am. Geophys. Union, 16th Ann. Meeting, pp.325~328.

Sheppard S.M.F. and Dawson J.B., $^{13}C/^{12}C$, $^{18}O/^{16}O$ and D/H isotope variations in "primary" igneous carbonatites. Fortsch. Mineral., 1973, 50: 128~129.

Schidlowski M., 1987, Application of stable isotopes to early biochemical evolution on earth. Ann. Rev. Earth Planet. Sci., 15, 47~72.

Schidlowski M., 1988, A 3800-million-year isotopic record of life from carbon in sedimentary rocks. Nature, 333, 313~318.

Schiffman P., Smith B.M., Varga R.J. and Moores E.M., 1987, Geometry, conditions and timing of off-axis hydrothermal metamorphism and ore-deposition in the Solea graben. Nature, 325, 425~425.

Schnetzler C.C. and Philpotts J.A., 1970, Partition coefficients of rare earth elements between igneous matrix material and rock-forming mineral phenocrysts — II. Geochim. Cosmochim. Acta, 34, 331~340.

Schock H.H., 1979, Distribution of rare-earth and other trace elements in magnetites. Chem. Geol., 26, 119~133.

Scotchman I.C., 1989, Diagnenesis of the Kimmeridge clay formation, onshore UK. J. Geol. Soc. Lond., 146, 285~303.

Searl A., 1988, Mixing-zone dolomites in the Gully Oolite, lower Carboniferous, south Wales. J. Geol. Soc. Lond., 145, 891~899.

Searl A., 1989, Diagenesis of the Gully Oolite (lower Carboniferous), south Wales. Geol. J., 24,275~293.

Seewald J.S. and Seyfried W.E., 1990, The effect of temperature on metal mobility in subseafloor hydrothermal systems: constraints from basalt alteration experiments. Earth Planet. Sci. Lett., 101, 388~403.

Shannon R.D., 1976, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallogr., Sect. A, 32, 751~767.

Sharp M.R., 1985, Strontium isotope evidence for preserved density stratification in the main zone of the Bushveld Complex, South Africa. Nature, 316, 119~126.

Sheppard S.M.P., 1977, The Cornubian Batholith, SW England: D/H and $^{18}O/^{16}O$ studies of kaolinite and other alteration minerals. J.Geol. Soc. Lond., 133, 573~591.

Sheppard S.M.P., 1981, Stable isotope geochemistry of fluids. In: Richard D.T. and Wickman F.E (eds.), *Chemistry and Geochemistry of solutions at high temperatures and pressures*, Phys. Chem. Earth 13/14, pp.419~445.

Sheppard S.M.P. and Schwartz H.P., 1970, Fractionation of carbon and oxygen isotopes and magnesium between metamorphic calcite and dolomite. Contrib. Mineral. Petrol., 26, 161~198.

Shervais J.W., 1982, Ti-V plots and the petrogenesis of modern and ophiolitic lavas. Earth Planet. Sci. Lett., 59, 101~118.

Shimizu N. and Hart S.R., 1982, Applications of the ion microprobe to geochemistry and coscochemistry. Ann Rev. Earth Planet. Sci., 10, 483~526.

Shirey S.B., Bender J.F. and Languir C.H., 1987, Three-component isotopic heterogeneity near the Oceanographer transform, Mid-Atlantic ridge. Nature, 325, 217~233.

Skala W., 1979, Some effects of the constant sum problem in geochemistry. Chem. Geol., 27, 1~9.

Skirrow R. and Coleman M.L., 1982, Origin of sulphur and geothermometry of hydrothermal sulphides from the Galapagos rift, 86)W. Nature, 299, 142~144.

Smalley P.C., Stijfhoorn D.E., Raheim A., Johansen /H. and Dickson J.A.D., 1989, The laser microprobe and its application to the study of C and O isotopes in calcite and aragonite. Sediment. Geol., 65, 211~221.

Smith R.E. and Smith S.E., 1976, Comments on the use of Ti, Zr, Y, Sr, K, P and Nb in classification of basaltic magmas. Earth Planet. Sci. Lett., 32, 114~120.

Song Y. and Frey F.A., 1989, Geochemistry of peridotite xenoliths in basalts from Hannuoba, eastern China: implications for sub-continental mantle heterogeneity. Geochim. Cosmochim. Acta, 53, 97~114.

Spooner E.T.C., Chapman H.J. and Smewing J.D., 1977, Strontium isotopic composition and oxidation during ocean floor hydrothermal metamorphism of the ophiolitic rocks of Troodos Mssif, Cyprus. Geochim. Cosmochim. Acta, 41, 873~890.

Spooner E.T.C. and Gale N.H., 1982, Pb-isotopic composition of ophiolitic volcanogenic sulphide deposits, Troodos Complex, Cyprus., 296, 239~242.

Stacey J.S. and Kramers J.D., 1975, Approximation of terrestrial lead isotope geochemistry of hydrothermally altered oceanic rocks. Earth Planet. Sci. Lett., 57, 285~304.

Stakes D.S. and O'Neil J.R., 1982, Mineralogy and stable isotope geochemistry of hydrothermally altered oceanic rocks. Earth Planet. Sci. Lett., 57, 285~304.

Staudigel H. and Bryan W.B., 1981, Contrasted glass-whole rock compositions and phenocryst redistribution, IPOD sites 417 and 418. Contrib. Mineral. Petrol., 78, 255~262.

Steiger R.H. and Jager E. , 1977, Subcommission on geochronology: convention of the use of decay constants in geo- and cosmochronology. Earth Planet. Sci. Lett., 36, 359~362.

Steiner J.C., Jahns R.H. and Luth W.C., 1975, Crystallisation of alkali feldspars and quartz in the haplogranite system $NaAlSi_3O_8$-$KAlSi_3O_8$-SiO_2-H_2O at 4 kb. Bull. Geol. Soc. Am., 86, 83~98.

Stille P., Unruh D.M. and Tatsumoto M, 1983, Pb, Sr, Nd and Hf isotopic evidence of multiple sources for Oahu, Hawwii basalts. Nature, 304, 25~29.

Storey M., Saunders A.D., Tarney J., Leat P., Thirlwall M.F., Thompson R.N., Menzies M.A. and Marriner G.F., 1988, Geochemical evidence for plume-mantle interactions beneath Kergulen and Herd Islands, Indian Ocean. Nature, 336, 371~374.

Stormer J.C. and Nicholls J., 1978, XLFRAC: A Program for the interactive testing of magmatic differentiation models. Computer Geosci., 4, 143~159.

Streckeisen A, 1976, To each plutonic rock its proper name. Earth Sci. Rev., 12, 1~33.

Streckeisen A. and Le Maitre R.W., 1979, A chemical approximation to the modal QAPF classification of igneous rocks. Neues Yahrb. Mineral. Abh., 136, 169~206.

Sun S.-S., 1980, Lead isotopic study of young volcanic rocks from mid-ocean ridges, ocean islands and island arcs. Phil. Trans. R. Soc. Lond., A297, 409~445.

Sun S.-S., 1982, Chemical composition and origin of the earth's primitive mantle. Geochim. Cosmochim. Acta, 46, 179~192.

Sun S.-S. and McDonough W.F., 1989, Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. In: Saunders A.D. and Norry M.J. (eds.), Magmatism in ocean basins. Geol. Soc. London. Spec. Publ. 42, pp.313~345.

Sun S.-S. and Nesbitt R.W., 1977, Chemical heterogeneity of the Archaean mantle, composition of the earth and mantle evolution. Earth Planet. Sci. Lett., 35, 429~448.

Sun S.-S., Wallace D.A., Hoatson D.M., Glikson A.Y. and Keays R.R., 1991, Use of geochemistry as a guide to platinum group element potential of mafic-ultramafic rocks: examples from the west Pilbara Block and Halls Creek Mobile Zone, Western Australia. Precamb. Res., 50, 1~35

Suzouki T. and Epstein S., 1976, Hydrogen isotope fractionation between OH-bearing minerals and water. Geochim. Cosmochim. Acta., 40, 1229~1240.

Tarney J., 1976, Geochemistry of Archaean high-grade gneisses, with implications as to the origin and evolution of the Precambrian crust. In: Windley B.F. (ed.), The early history of the earth. New York: Wiley, pp.405~418.

Tatsumoto M, Knight R.J. and Allegre C.J., 1973, Time difference in the formation of meteorites as determined from the ratio of lead-207 to lead-206. Science,180, 1279~1283.

Taylor D. and MacKenzie W.S., 1975, A contribution to the pseudoleucite problem. Contrib. Mineral Petrol., 49, 321~333.

Taylor H.P., 1974, The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposit. Econ. Geol., 69, 843~883.

Taylor H.P., 1977, water/rock interactions and the origin of H_2O in granitic batholiths. J. Geol. Soc. Lond., 133, 509~558.

Taylor H.P., 1978, Oxygen and hydrogen isotope studies of plutonic granitic rocks. Earth Planet. Sci. Lett., 38, 177~210.

Taylor H.P., 1979, Oxygen and hydrogen isotope relationships in hydrothermal mineral deposits. In: Barnes H.L.(ed.), Geochemistry of hydrothermal ore deposits. 2nd edition. New York: Wiley, pp.236~277.

Taylor H.P. and Epstein S., 1962, Relationships between ^{18}O and ^{16}O ratios in coexisting minerals of igneous and metamorphic rocks. Part 2 Application to petrologic problems. Geol. Soc. Am. Bull., 73, 675~694.

Taylor P.N., Jones N.W. and Moorbath S.,1984, Isotopic assessment of relative contributions from crust and mantle sources to magma genesis of Precambrian granitoid rocks. Phil. Trans. R. Soc. Lond., A310, 605~625.

Taylor P.N., Moorbath S., Goodwin R. and Petrykowski A.C., 1980, Crustal contamination as an indicator of the extent of early Archaean continental crust: Pb isotopic evidence from the late Archaean gneisses of west Greenland. Geochim. Cosmochim Acta, 44, 1437~1453.

Taylor R.P. and Fryer B.J., 1980, Multi-stage hydrothermal alteration in porphyry copper systems in northern Turkey: the temporal interplay of potassic, propylitic and phyllic fluids. Can. J. Earth Sci., 17, 901~926.

Tayloy S.R. and Mclennan S.M., 1981, The composition and evolution of the continental crust: rare earth element evidence from sedimentary rocks. Phil. Trans. R. Soc. London, A301, 381~399.

Tayloy S.R. and Mclennan S.M., 1985, *The continental crust: its compositiom and evolution.* Oxford: Blackwell

Tertian R. and Claisse F., 1982, Principles of quantitative X-ray fluorescence analysis. New York: Wiley-Heyden.

Thode H.G. and Monster J., 1965, Sulfur isotope geochemistry of petroleum, evaporites and ancient seas. Am. Assoc. Pet. Geol. Mem., 4, 367~377.

Thompson M. and Walsh J.N., 1983, *A handbook of inductively coupled plasma spectrometry.* Glasgow: Blackie.

Thompson R.N., 1982, British Tertiary volcanic province. Scott. J. Geol., 18, 59~107.

Thompson R.N., 1984, Dispatches from the basalt front. I. Experiments. Proc. Geol. Ass., 95, 249~262.

Thompson R.N., 1987, Phase equilibria constraints on the genesis and magmatic evolution of oceanic basalts. Earth Sci. Rev., 24, 161~210.

Thompson R.N., Morrison M.A., Dickin A.P. and Henry G.L., 1983, Continental flood basalts... Arachnids rule OK? In: Hawkesworth C.J. and Norry M.J. (eds.), Continental basalts and mantle xenoliths. Nantwich: Shiva, pp., 158~185.

Thompson R.N., Morrison M.A., Hentry G.L. and Parry S.J., 1984, An assessment of the relative roles of crust and mantle in magma genesis: an elemental approach. Phil. Trans. R. Soc. London, A310, 549~590.

Till R., 1974, *Statistical methods for the earth scientist: an introduction.* Oxford: Macmillan.

Till R., 1977, The HARDROCK package, a series of FORTRAN IV computer programs for performing and plotting petrochemical calculation. Computer Geosci., 3, 185~243.

Tilton G.R., 1973, Isotopic lead ages of chondritic meteorites. Earth Planet. Sci. Lett., 19, 321~329.

Topley C.G. and Burwell A.D. M., 1984, Triplot: an interactive program in basic for plotting triangular diagrams. Computer Sci., 10, 277~309.

Treuil M. and Varet J., 1973, Criteres volcanologiques, petrolgiques et geochimique de la genese et de la differenciation des magmas basaltique: exemple de l'Afar. Bull. Geol. Soc. France, 7th ser., 15, 401~644.

Troutman B.M. and Williams G.P., 1987, Fitting straight lines in the earth sciences. In: Studies in mathematical geology 1. Oxford: Oxford Univ. Press, pp.107~128.

Trudinger P.A., Chambers L.A. and Smith J.W., 1985, Low-temperature sulphate reduction: biological vs abiological. Can. J. Earth Sci., 22, 1910~1918.

Tuttle O.F. and Bowen N.L., 1958, The origin of granite in the light of experimental studies suites in the system $NaAlSi_3O_8$-K $AlSi_3O_8$-SiO_2-H_2O. Mem. Geol. Soc. Am, No.74.

Twist D. and Harmer R.E.J., 1987, Geochemistry of contrasting siliceous magmatic suites in the Bushveld Complex: genetic aspects and implications for tectonic discrimination diagrams. J. Volc. Geothermal Res., 32,

83098.

Ueda A. and Sakai H., 1984, Sulfur isotope study of Quaternary volcanic rocks from the Japanese islands arc. Geochim. Coscochim. Acta, 48, 1837~1848.

Urey H.C., 1947, The thermodynamic properties of isotopic substance. J. Chem. Soc., 562~581.

Valley J.W. and O'Neil J.R., 1981, 13C/12C exchange between calcite and graphite: a possible thermometer in Grenville marbles. Geochim. Coscochim. Acta, 48, 1837~1848.

Valley J W. and O'Neil J.R., 1984, Fluid heterogeneity during ganulite facies metamorphism in the Adirondacks: stable isotope evidence. Contrib. Mineral. Petrol., 85, 158~173.

Valley J.W., Taylor H.P. and O'Neil J.R., 1986, Stable isotopes and high temperature geological processes. Rev. Mineral., 16.

van Breemen O., Aftalion M., Pankhurst R.J. and Richardson S.W., 1979, Age of the Glen Gessary syenite, Invernessshire: Diachronous Palaeozoic metamorphism across the great Glen. Scot. J. Geol., 15, 49~62.

Vance D., Stone J.O.H. and O'Nions R.K., 1989, He, Sr and Nd isotopes in xenoliths from Hawaii and other oceanic islands. Earth Planet. Sci. Lett., 96, 147~160.

Veizer J., 1989, Strontium isotopes in seawater through time. Ann. Rev. Earth Planet. Sci., 17, 141~167.

Veizer J., Fritz P. and Jones B., 1986, Geochemistry of brachiiopods: oxygen and carbon isotopic records of Paleozoic oceans. Geochim. Cosmochim. Acta, 50, 1679~1696.

Verma M.P., 1986, A program package for major element data handling and CIPW norm calculation. Computer Geosci., 12, 381~399.

Vernon R.H., Flood R.H. and D'Arcy W.F., 1987, Sillimanite and andalusite produced by base-cation leaching and contact metamorphism of felsic igneous rock. J. Metemorphic Geol., 5, 439~450.

Vidal Ph. and Clauer N., 1981, Pb and Sr isotopic systematics of some basalts and sulfides from the East Pacific Rise at 21° N (project RITA). Earth Planet. Sci. Lett., 55, 237~246.

Vitrac A.M., Albarede F. and Allegre C.J., 1981, Lead isotopic composition of Hercynian granitite K-feldspars constrains continental genesis. Nature, 291, 460~464.

Wada H. and Suzuki K., 1983, Carbon isotope thermometry calibrated by dolomite-calcite solvus temperatures. Geochim. Cosmochim. Acta, 47, 697~706.

Wainerdi R.E. and Uken E. A., 1971, *Modern methods of geochemical analysis*. New York: Plenum Press.

Wakita H., Rey P. and Schmitt R.A., 1971, Abundances of the 14 rare-earth elements and 12 other trace elements in Apollo 12 samples: five igneous and one breccia rocks and four soils. Proc. 2nd Lunar Sci. Conf. Oxford: Peramon Press, pp.1319~1329.

Walker D., Shibata T. and DeLong S.E., 1979, Abyssal tholeiites from the Oceanographer Fracture Zone III. Phase equilibria and mixing. Contrib. Mineral. Petrol., 70, 111~125.

Walsh J.N., Buckley F. and Barker J., 1981, The simultaneous determination of the rare-earth elements in rocks using inductively coupled plasma source spetrometry. Chem. Geol., 33, 141~153.

Walsh J.N. and Howie R.A., 1980 An evaluation of the performance of an inductively coupled plasma source

spectrometer for determination of major and trace constituents of silicate rocks and minerals. Mineral. Mag., 47, 967~974.

Wasserburg G.J., Jacoben S.B., DePaolo D.J., McCulloch M.T. and Wen J., 1981, Precise determinations of Sm/Nd ratios, Sm and Nd isotopic abundances in standard solutions. Geochim. Cosmochim. Acta, 45, 2311~2323.

Watson E.B., 1976, Two-liquid partition coefficients: experimental data and geochemical implications. Contrib. Mineral. Petrol., 56, 119~134.

Watson E.B. and Harrison M.T., 1983, Zircon saturation revisited: temperature and composition effects in a variety of crustal magma types. Earth Planet. Sci. Lett., 64, 295~304.

Watson E.B. and Ryerson F.J., 1986, Partitioning of zircon between clinopyroxene and magmatic liquids of intermediate composition. Geochim. Cosmochim. Acta, 50, 2523~2526.

Weaver B.L., 1991. The origin of ocean island basalt end-member compositions: trace element and isotopic constraints. Earth Planet. Sci., 104, 3810.

Weaver B.L. and Tarney J., 1984, Empirical approach to estimating the composition of the continental crust. Nature, 310, 575.

Weaver B.L., Tarney J. and Windley B., 1981, Geochemistry and petrogenesis of the Fiskenaesset anorthosite complex southern West Greenland: nature of the parent magma. Geochim. Cosmochim. Acta, 45, 711~725.

Weaver S.D., 1987, Introduction. In: Weaver S.D. and Johnstone R.W. (eds.), *Tectonic controls on magmachemistry. J. Volc. Geothermal Res.*, ix-x.

Whelan J.F., Cobb J.C. and Rye R.O., 1988, Stable isotope chemistry of sphalerite and other mineral matter in coal beds of the Illinois and Forest City basins. Econ. Geol., 83, 990~1007.

White W M. and Hofmann A.W., 1982, Sr and Nd isotope geochemistry of oceanic basalts and mantle evolution. Nature, 296, 821~825.

White W.M and Patchett J., 1984, Hf-Nd-Sr isotopes and incompatible element abundances in island arcs: implications for magma origins and crust-mantle evolution. Earth Planet. Sci. Lett., 67, 167~185.

Whitehouse M.J., 1989a, Sm-Nd evidence for diachronous crustal accretion in the Lewsian complex of northwes Scotland. Tectonophysics, 161, 245~256.

Whitehouse M.J., 1989a, Pb-isotopic evidence for U-Th-Pb behaviour in a prograde amphibole to granulite facies transition from the Lewisian complex of north-west Scotland: implications for Pb-Pb dating. Geochim. Cosmochim. Acta, 53, 717~724.

Wickham S.M., 1988, Evolution of the lower crust. Nature, 333, 119~120.

Wickham S.M. and Taylor H.P., 1985, Stable isotope evidence for large-scale seawater infiltration in a regional metamorphic terrane: the Trois Seigneus Massif, Pyrenees, France. Contrib. Mineral. Petrol., 91, 122~137.

Wilkinson J.F.G., 1982, The genesis of mid-ocean ridge basalt. Earth Sci. Rev. 18, 1~57.

Williams D.F., Lerche I. and Full W.E., 1988, Isotope chronostratigraphy: theory and methods. San Diego: Academic Press.

Williams G.P., 1983, Improper use of regression equations in earth sciences. Geology, 11, 195~197.

Williams K.L., 1987, *Introduction to X-ray spectrometry*. London: Allen and Unwin.hydrogen isotope

Wilson M., 1989, Igneous petrogenesis. London: Allen and Unwin.

Winchester J.A. and Floyd P.A., 1976, Geochemical magma tyoe discriminations; application to altered and metamorphosed basic igneous rocks. Earth Planet. Sci. Lett., 28, 459~469.

Winchester J.A. and Floyd P.A., 1977, Geochemical discrimination of different magma series and their differentiation products using immobile elements. Chem. Geol., 20, 325~343.

Winchester J.A. and Max M.D., 1989, Tectonic setting discrimination in clastic sequences: an example from the late Proterozoic Erris group, NW Ireland. Precamb. Res., 45, 191~201.

Windrim D.P and McCulloch M.T., 1986, Nd and Sr isotopic systematics of central Australian granulites: chronology of crustal development and constraints on the volume of the lower continental crust. Contrib. Minerla. Petrol., 94, 289~303.

Winkler H.G.F., 1976, Petrogenesis of metamorphic rocks, 4th edition. New York: Springer.

Wood D.A., 1980, The application of a Th-Hf-Ta diagram to problems of tectonomagmatic classification and to establishing the nature of crustal contamination of basaltic lavas of the British Tertiary volcanic province. Earth Planet. Sci. Lett., 50, 11~30.

Wood D.A., Joron J.L., Treuil M., Norry M.J. and Tarney J., 1979a, Elemental and Sr isotope variations in basic lavas from Iceland and the surrounding ocean floor. Contrib. Minerla. Petrol., 70, 319~339.

Wood D.A., Tarney J., Varet J., Saunders A.D., Bougault H., Joron J.L., Treuil M. and Cann J.R., 1979b, Geochemistry of basalts drilled in the North Atlantic by IPOD Leg 49: implications for mantle heterogeneity. Earth Planet. Sci. Lett., 42, 77~97.

Wood D.A., Joron J.L. and Treuil M, 1979c, A re-appraisal of the use of trace elements to classify and discriminate between magma series erupted in deferent tectonic settings. Earth Planet. Sci. Lett., 45, 326~336.

Wood D.A., Tarney J. and Weaver B.L., 1981, Trace element variations in Atlantic ocean basalts and Proterozoic dykes from Northwest Scotland: their bearing upon the nature and geochemical evolution of the upper mantle. Tectonophysics, 75, 91~112.

Woodhead J.D., Harmon R.S. and Fraser D.G., 1987, O, S, Sr and Pb isotope variations in volcanic rocks from the Northern Mariana islands: implications for crustal recycling in intra-oceanic arcs. Earth Planet. Sci. Lett., 83, 39~52.

Woodruff L.G. and Shanks W.C., 1988, Sulfur isotope study of chimney minerals and vent fluid from 21°N, East Pacific Rise: hydrothermal sulfur sources and disequilibrium sulfate reduction. J. Geophys. Res., 93, 4562~4572.

Woronow A., 1990, Methods for quantifying, statistically testing and graphically displaying shifts in compositional abundances across data suits. Computer Geosci., 16, 1209~1233.

Woronow A., 1991, Endmember unmixing of compositional data. Geochim. Cosmochim. Acta, 55, 2351~2353.

Woronow A. and Butler J.C., 1986, Complete subcompositional independence testing of closed arrays. Compueter Sci., 12, 267~279.

Woronow A. and Love K.M, 1990, Quantifying and testing differences among means of compositional data. Math. Geosci., 22, 838~852.

Wright I.P., Grady M.M. and Pillinger C.T., 1988, Carbon, oxygen and nitrogen isotopic composition of possible martian weathering products in EETA 79001. Geochim. Cosmochim. Acta, 52, 917~924.

Wright T.L., 1974, Presentation and interpretation of chemical data for igneous rocks. Contrib. *Minerla. Petrol.*,

48, 233~248.

Wright T.L., and Doherty P.C., 1970, A linear programming and least squares computer method for solving petrologic mixing problems. Geol. Soc. Am. Bull., 81, 1995~2008.

Wronkiewicz D.J. and Condie K.C., 1987, Geochemistry of Archaean shales from the Witatersrand Supergroup, South Africa: source-area weathering and provenance. Geochim Cosmochim. Acta, 51, 2401~2416.

Yorder H.S. and Tilley C.E., 1962, Origin of basalt magmas: an experimental study of natural and synthetic rock systems. J. Petrol., 3, 342~532.

York D., 1967, The best isochron. Earth Planet. Sci. Lett., 2, 479~482.

York D., 1969, Least squares fitting of a straight line with correlated errors. Earth Planet. Sci. Lett., 5, 320~334.

Zachmann D.W., 1988, Matrix effects in the separation of rare earth elements, scandium and yttrium and their determination by inductively coupled plasma emission spectrometry. Anal. Chem., 60, 420~427.

Zarman R.E. and Haines S.M., 1988, The plumbotectonic model for Pb isotopic systematics among major terrestrial reservoirs — a case for bidirectional transport. Geochim. Cosmochim. Acta, 52, 1327~1339.

Zheng Y.-F., 1990, The effect of Rayleigh degassing of a magma on sulphur isotope composition: a quantitative evaluation. Terra Nova, 2,74~78.

Zhou Di, 1987, Robust statistics and geochemical data analysis. J. Math. Geol., 19, 207~218.

Zindler A. and Hart S.R., 1986, Chemical geodynamics. Ann. Rev. Earth Planet. Sci., 14, 493~571.

Zindler A., Jagoutz E. and Goldstein S., 1982, Nd, Sr and Pb isotopic systematics in a three-component mantle: a new perspective. Nature, 298, 519~523.