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MICRO-ANALYTICAL TECHNIQUES IN STABLE-ISOTOPE GEOCHEMISTRY

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ABSTRACT

Novel analytical techniques involving the use of secondary-ion mass spectroscopy (SIMS) and lasers are currently being developed for the measurement of the H, C, N, O and S isotopic composition of rocks and minerals. SIMS has been used for *in situ* analysis of the H, C, O and S isotopic composition of minerals, with excellent spatial resolution of *ca.* 10 μm, but uncertainties of *ca.* 10–20 times greater than conventional analyses. Laser-assisted analyses have been reported for C and O in calcite, O in mafic silicates and quartz, and S in sulfides. These techniques normally use the laser as a way of heating a small area of the sample (*i.e.*, >50 μm in diameter), so that the effectiveness of the laser depends on the manner in which the laser energy is absorbed by the mineral. Most systems use a CO_2 laser, which has a wavelength of 10.6 μm that is at least partially absorbed by most minerals, or a Nd:YAG laser, which has a wavelength of 1.064 μm that is absorbed primarily by *d*-orbital electrons in transition metals. The energy from UV lasers is absorbed efficiently by most minerals, although as with all types of laser, the energy affects each mineral differently depending on its chemical composition and crystal structure. Two consequences of the differential absorption of laser energy by minerals are: (1) variations in the chemical compositions of most samples can result in significant fractionations of isotopes, and (2) differential absorption makes *in situ* analysis difficult because the uneven distribution of the energy can result in partial extraction of the element of interest. Many researchers have attached laser and extraction systems directly to high-sensitivity mass spectrometers, thus permitting analysis of smaller samples than was realized using conventional techniques. This has been the most significant contribution of the use of lasers to isotope geochemistry to date, although successful and more reliable *in situ* analysis using UV or other types of lasers may be forthcoming.

Keywords: stable isotopes, laser, secondary-ion mass spectrometry, absorption spectra, micro-analysis.

SOMMAIRE

Des techniques analytiques nouvelles impliquant la spectrométrie de masse des ions secondaires (SIMS) avec ablation au laser sont en voie de développement pour mesurer la composition isotopique (H, C, N, O et S) des roches et des minéraux. La technique SIMS a été utilisée pour l'analyse *in situ* des rapports des isotopes de H, C, O et S des minéraux, avec une résolution spatiale impressionante de 10 μm, mais avec une erreur expérimentale de 10 à 20 fois celle des analyses conventionnelles. Des résultats d'analyses par ablation au laser ont été décrits pour les isotopes de C et de O dans la calcite, ceux de O dans les silicates mafiques et le quartz, et ceux de S dans les sulfures. La technique employée normalement se sert du laser pour chauffer un petit domaine du minéral (>50 μm de diamètre), de telle sorte que l'efficacité du laser dépend de la façon dont est absorbée l'énergie. La plupart des systèmes se servent d'un laser au CO_2, qui possède une longueur d'onde de 10.6 μm, absorbée au moins en partie par la plupart des minéraux, ou un laser au Nd:YAG, qui possède une longueur d'onde de 1.064 μm, absorbée en grande partie par les électrons *d* des métaux de transition. L'énergie provenant d'un laser UV est absorbée efficacement par la plupart des minéraux, mais comme tous les types de laser, l'énergie affecte chaque minéral de façon différente selon sa composition chimique et sa structure cristalline. Il y a deux conséquences de l'absorption différentielle de l'énergie du laser par les minéraux: (1) les variations en composition chimique de la plupart des échantillons peuvent mener à un fractionnement important des isotopes, et (2) l'absorption différentielle rend l'analyse *in situ* difficile parce que la distribution inégale de l'énergie peut provoquer une extraction partielle de l'élément d'intérêt. La plupart des chercheurs ont rattaché le laser et le système d'extraction directement à leur spectromètre de masse à sensibilité élevée, permettant ainsi l'analyse d'échantillons plus petits qu'ils ne pourraient réaliser par techniques conventionnelles. C'est cet avantage qui est la contribution la plus importante de l'application d'un rayon laser en géochimie isotopique à date, quoiqu'il est possible de prévoir des analyses *in situ* plus fiables et plus réussies avec un laser UV ou un autre type de laser.

(Traduit par la Rédaction)

Mots-clés: isotopes stables, laser, spectrométrie de masse des ions secondaires, spectres d'absorption, micro-analyse.

INTRODUCTION

Conventional analysis of the stable-isotope compositions of natural materials normally involves extraction of a gas containing the element of interest from several milligrams of sample (*e.g.*, Kyser 1987). In addition to requiring a significant quantity of sample, conventional analysis is done using specialized extraction lines and reagents, after which the purified gases are transferred to an isotope-ratio mass spectrometer. Advances in techniques of mass spectrometry have permitted the accurate analysis of small quantities of gas (*i.e.*, a few micromoles), but improvements in extraction techniques and sample preparation have only recently been able to capitalize on these advances. Within the past four years, laser-assisted extraction of gases from natural samples and secondary-ion mass spectrometry (SIMS) have shown promise for micro-analysis of the stable-isotope composition of small samples of rocks and minerals. However, these novel analytical techniques do have severe limitations that are just beginning to be recognized and understood. It is the purpose of this paper to review recently developed micro-analytical techniques in stable-isotope geochemistry and to compare and contrast the advantages and limitations of each technique.

METHODS USED FOR STABLE-ISOTOPE ANALYSIS

Presently, there are three methods normally used to measure the stable-isotope composition of small samples of rocks and minerals: (1) "conventional" techniques, which use a multitude of reagents to extract the element of interest from the sample, normally with extraction lines removed from the inlet system of the mass spectrometer, (2) SIMS, which uses a Cs^+ beam to make H_2^+, C, O^- or S^- *in situ*, and (3) laser-assisted analysis, which uses a laser to heat the sample in the presence of a reagent, if required.

Conventional analysis has been the mainstay of stable-isotope geochemistry since its inception, and improvements have generally involved simpler techniques and more efficient reaction vessels so that smaller quantities of sample could be analyzed (Table 1). In most cases, the analysis of sulfides, carbonates, silicates and oxides requires more than 1 mg of sample, and *in situ* analysis is not possible using conventional techniques. Many laboratories have miniaturized their extraction lines and connected them directly to the inlet system of the mass spectrometer to improve the precision and accuracy of analysis for small samples, (*i.e.*, 0.1–1 mg). Some minerals, such as olivine, kyanite and garnet, do not react well with the fluorinating reagents used, although the $\delta^{18}O$ value of these minerals is not dependent on the yield of oxygen obtained (Kyser *et al.* 1981). The accuracy and precision for most conventional methods of analysis of C, N, O, and S isotopes are ±0.2‰; corresponding values for the analysis of the H-isotope composition of silicates are ±3‰.

SIMS uses a Cs^+ primary-ion beam to ablate the surface of a sample located near the ion source of a mass spectrometer (*e.g.*, Chaussidon *et al.* 1989, Deloule *et al.* 1991, Valley & Graham 1993). This analysis is done *in situ* with a spatial resolution of less than 10 µm (Table 1). Variations in the character of the primary ion beam and interaction of the sample with the beam result in extreme isotopic fractionations (*ca.* several hundred ‰) that are sample-dependent, and require substantial corrections to the measured ratios.

TABLE 1. CHARACTERISTICS OF DIFFERENT METHODS FOR ANALYSIS OF THE OXYGEN-ISOTOPE COMPOSITION OF SILICATES, OXIDES AND CARBONATES

Method	Procedure	Quantity Required	Spatial Resolution	Precision	Comment
Conventional	react sample with BrF_5 or ClF_3 in Ni vessel at 600 °C to release O_2; react carbonates with 100% H_3PO_4	>1mg	n.a.	<0.2 ‰	olivine, kyanite do not react well, but $\delta^{18}O$ is not dependent on yield
Laser-assisted	samples heated by CO_2 or Nd-YAG laser for carbonates and in presence of BrF_5 or ClF_3 for silicates and oxides	>1 mg or "special" corrections may be required	<200 µm	silicate and oxide separates, >0.3‰; *in situ*, variable but >0.4‰; carbonates require corrections because of incomplete extraction	very dependent on yield of O_2 extracted from silicates and oxides; all values are dependent on chemical composition of sample
Ion Probe	Cs^+ primary beam	75 µm^3	<10 µm	>2.0 ‰	used for *in situ* analysis, but fractionations are extreme and mineral-dependent; no data on carbonates

As a result of these corrections and fluctuations in the energy of the ion beam, the precision of the results are typically ± several ‰, an order of magnitude more than conventional methods of analysis.

Laser-assisted techniques can be considered as variations on conventional methods of analysis in that the laser serves as a source of heat, albeit a focused source (Table 1). Carbonates are heated or ablated directly with a beam from a CO_2 or Nd:YAG laser, and the resulting CO_2 is analyzed (*e.g.*, Smalley *et al.* 1989, Powell & Kyser 1991). Depending on the type of carbonate or the laboratory in which the analysis is done, special corrections are required because only about two-thirds of the oxygen is extracted. Silicates and oxides are heated by laser beam in the presence of BrF_5, F_2 or ClF_3, and the O_2 released normally is reacted with carbon to make CO_2, which then is analyzed (*e.g.*, Sharp 1990, Elsenheimer & Valley 1992, Mattey & Macpherson 1993). The values obtained using the laser on pure mineral separates compare favorably with results from conventional analysis, depending on the mineral analyzed. As will be discussed, the accuracy of laser-assisted analysis of pure mineral separates depends markedly on the yield of gas extracted. *In situ* analysis using the laser gives results of variable precision, usually at least twice that obtained for pure mineral separates. Although most results from laser-assisted analysis are reported with precisions of only 1σ, all uncertainties discussed in this paper have been adjusted to 2σ, in conformity with current practice in conventional analysis.

TECHNIQUES OF LASER-ASSISTED EXTRACTION

Absorption characteristics

The basic premise of laser-assisted extraction of specific elements from rocks and minerals is that the energy from the laser beam is absorbed efficiently and reproducibly by the sample. A substance will absorb energy from the laser depending on the absorption characteristics of the sample at the wavelength of the laser (Fig. 1). The energy from the laser can be absorbed in a variety of ways by the mineral, such as by the framework anions, the cations and by defects. Depending on how the energy is dissipated from the area where the beam impinges on the sample, the volume affected by the energy of the laser may be several times larger than the volume directly impinged by the beam. For example, a reaction front may develop as the energy is dissipated from the area of impingement. Although less critical for analysis of mineral separates because all of the sample can be affected more or less equally by the laser energy as the beam is rastered, the differential absorption characteristics of large samples can render *in situ* analysis problematic.

CO_2 lasers

The most commonly used lasers in stable isotope geochemistry are CO_2 lasers, which have an effective wavelength near 10.6 μm. As with most lasers, the wavelength can be varied somewhat, typically by up to ±10%. The wavelength of CO_2 lasers is nearly coincident with a fundamental vibration of $(CO_3)^{2-}$ and, as such, the energy from CO_2 lasers should be absorbed in nearly the same way in most carbonates (Fig. 1). Most silicate minerals also have an absorption peak near the wavelength of CO_2 lasers, corresponding to the frequency of principal stretching of the (SiO_4) group. However, the exact location of this absorption depends on the connectivity of the (SiO_4) groups (Fig. 1). Therefore, the absorption efficiency of energy from a CO_2 laser differs between silicates and carbonates, with the degree of absorption for silicates being very dependent on crystal structure and chemical composition. Furthermore, the beam diameter of most CO_2 lasers is 20–50 μm, but the area affected can be substantially greater, thus limiting the spatial resolution of *in situ* analyses.

Nd:YAG lasers

Nd:YAG and Nd-glass lasers are also used for laser-assisted extractions, and both have wavelengths of 1.064 μm in the infrared (IR) part of the spectrum (Fig. 1). This wavelength corresponds to electronic transitions in *d* orbitals of third-row transition-metals, so that the efficiency of absorption of the energy from a Nd:YAG laser depends primarily on the concentration of transition metals. This is true for both carbonates and silicates; mafic silicates and Fe–Mn carbonates readily absorb the energy from Nd:YAG lasers (Fig. 1). Most sulfides readily absorb energy from Nd-type lasers because of their high transition-element content, although the efficiency of absorption depends greatly on which transition elements are present (Fig. 1). The coincidence of the wavelength of Nd-type lasers with electronic transitions within transition metals such as Fe^{2+} renders the absorption characteristics extremely dependent on the chemical composition of the sample. Therefore, the absorption efficiency of different samples is unlikely to be the same unless the transition-element contents are similar.

The wavelength of Nd-type lasers can be altered *via* frequency doubling, resulting in energy of 0.532 μm in the near-IR region, or quadrupling, which produces a wavelength of 0.266 μm in the ultraviolet (UV) region. The effective beam-diameter of Nd-type lasers approaches 10 μm, although the area affected by the laser energy is normally much greater (Powell & Kyser 1991, Elsenheimer & Valley 1992, Fallick *et al.* 1992, Kelley *et al.* 1992). Most silicates, carbonates and sulfides readily absorb energy of UV wavelengths (Fig. 1), although the effect of differential efficiencies

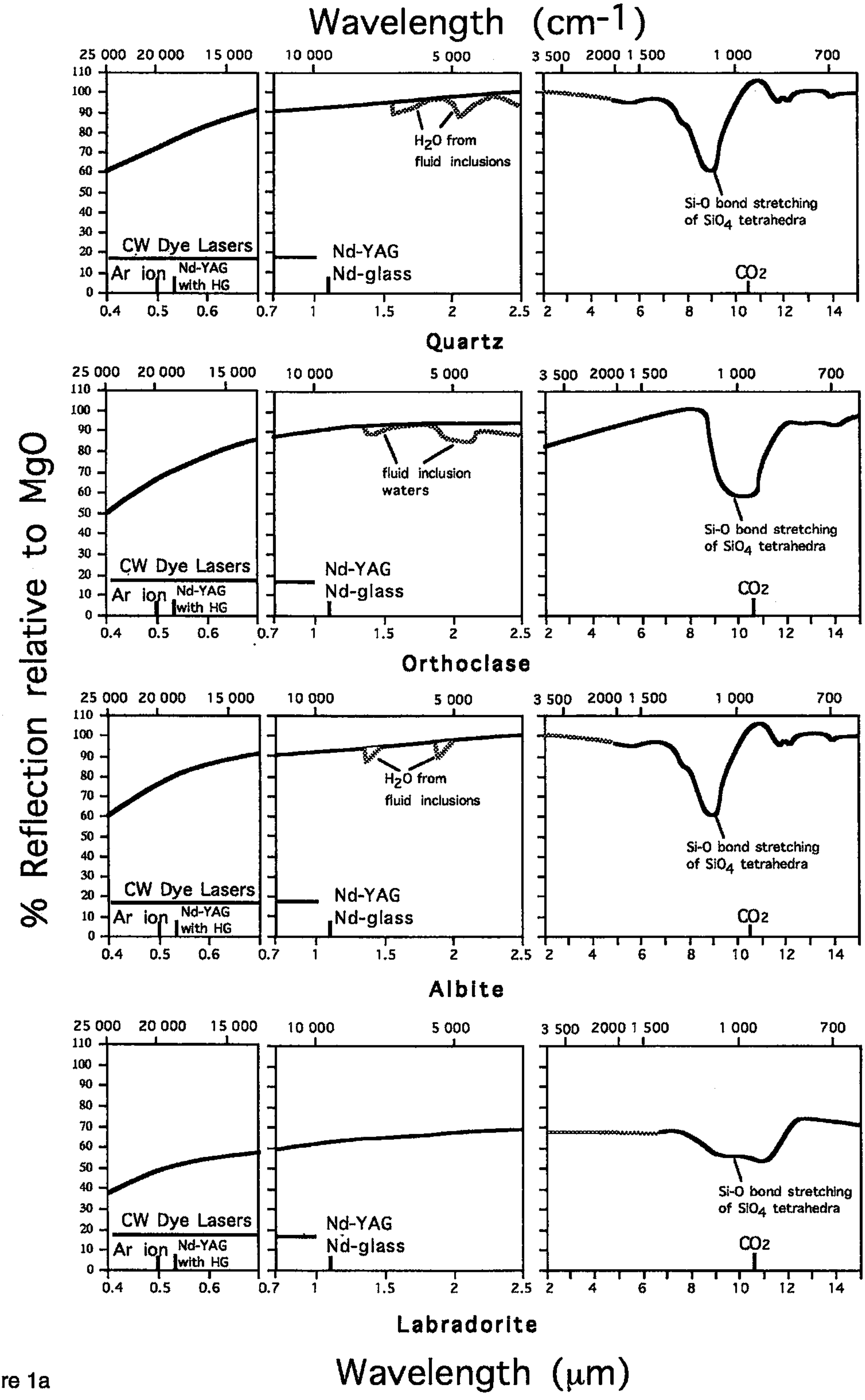
Wavelength (cm-1)
% Reflection relative to MgO
25 000
20 000
15 000
10 000
5 000
3 500
2000
1 500
1 000
700
CW Dye Lasers
Ar ion
Nd-YAG with HG
Nd-YAG
Nd-glass
H_2O from fluid inclusions
fluid inclusion waters
Si-O bond stretching of SiO_4 tetrahedra
CO2
Quartz
Orthoclase
Albite
Labradorite
Wavelength (μm)

Figure 1a

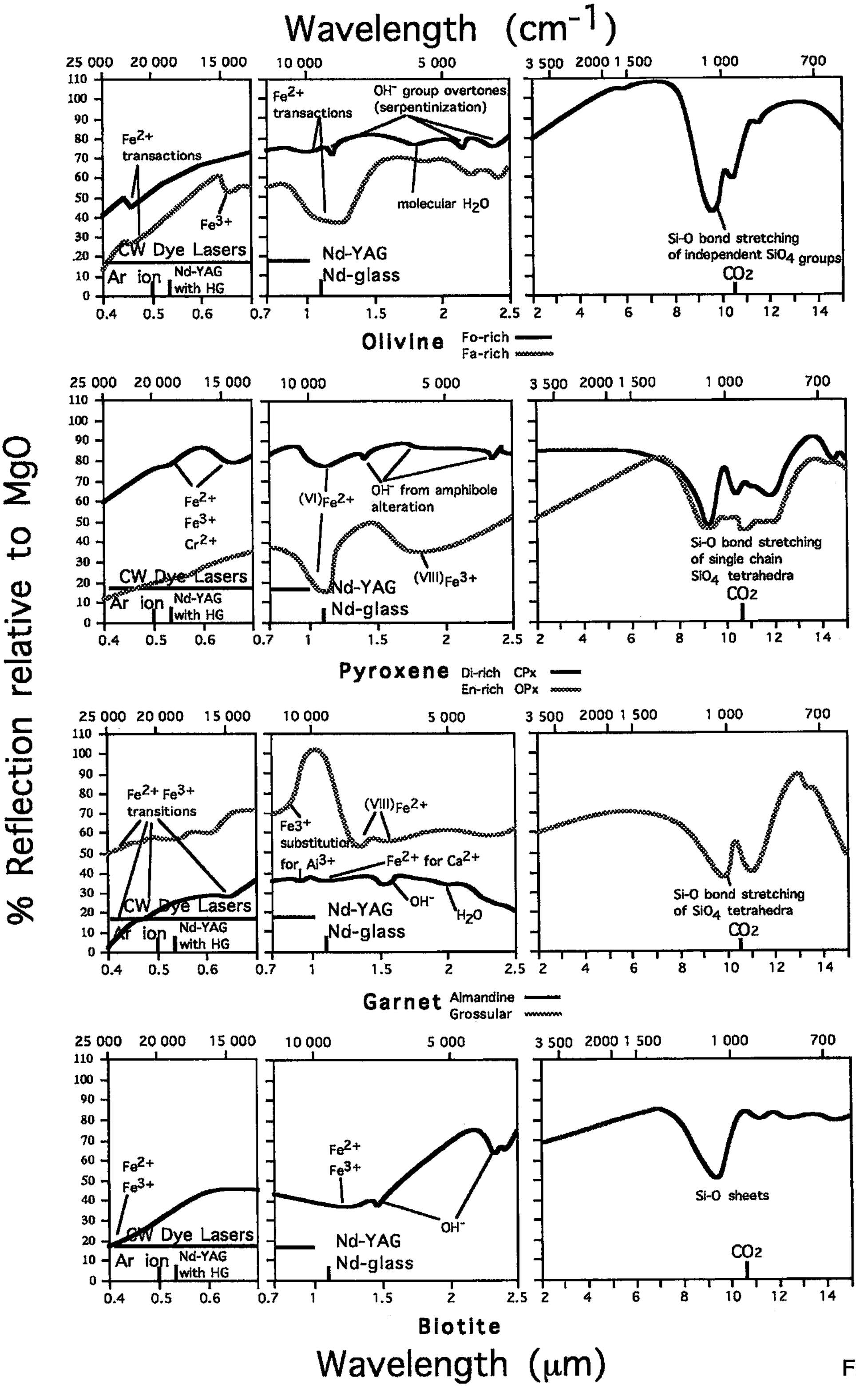
Wavelength (cm^{-1})
25 000
20 000
15 000
10 000
5 000
3 500
2000
1 500
1 000
700
% Reflection relative to MgO
0
10
20
30
40
50
60
70
80
90
100
110
Fe^{2+} transactions
Fe^{3+}
CW Dye Lasers
Ar ion
Nd-YAG with HG
Fe^{2+} transactions
OH$^-$ group overtones (serpentinization)
molecular H_2O
Nd-YAG
Nd-glass
Si-O bond stretching of independent SiO_4 groups
CO2
0.4
0.5
0.6
0.7
1
1.5
2
2.5
2
4
6
8
10
12
14
Olivine
Fo-rich
Fa-rich
Fe^{2+}
Fe^{3+}
Cr^{2+}
$^{(VI)}Fe^{2+}$
OH$^-$ from amphibole alteration
$^{(VIII)}Fe^{3+}$
Si-O bond stretching of single chain SiO_4 tetrahedra
Pyroxene
Di-rich CPx
En-rich OPx
Fe^{2+} Fe^{3+} transitions
Fe^{3+} substitution for Al^{3+}
$^{(VIII)}Fe^{2+}$
Fe^{2+} for Ca^{2+}
OH$^-$
H_2O
Si-O bond stretching of SiO_4 tetrahedra
Garnet
Almandine
Grossular
Fe^{2+}
Fe^{3+}
OH$^-$
Si-O sheets
Biotite
Wavelength (µm)

Figure 1b

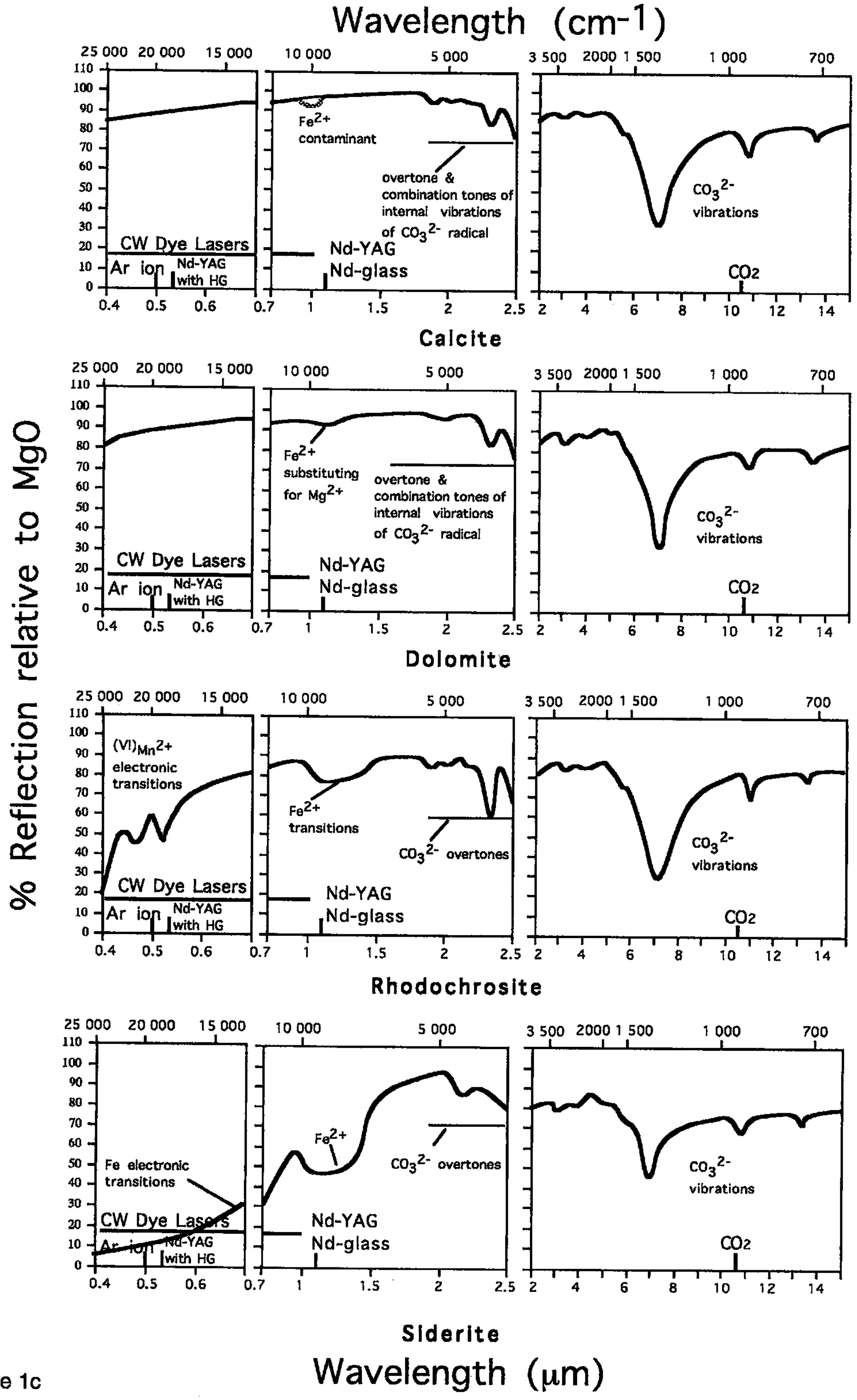
Wavelength (cm-1)
% Reflection relative to MgO
25 000
20 000
15 000
10 000
5 000
3 500
2000
1 500
1 000
700
110
100
90
80
70
60
50
40
30
20
10
0
0.4
0.5
0.6
0.7
1
1.5
2
2.5
4
6
8
10
12
14
CW Dye Lasers
Ar ion
Nd-YAG with HG
Nd-YAG
Nd-glass
CO2
Fe2+ contaminant
overtone & combination tones of internal vibrations of CO3 2- radical
CO3 2- vibrations
Calcite
Fe2+ substituting for Mg2+
Dolomite
(VI)Mn2+ electronic transitions
Fe2+ transitions
CO3 2- overtones
Rhodochrosite
Fe electronic transitions
Fe2+
Siderite
Wavelength (μm)

Figure 1c

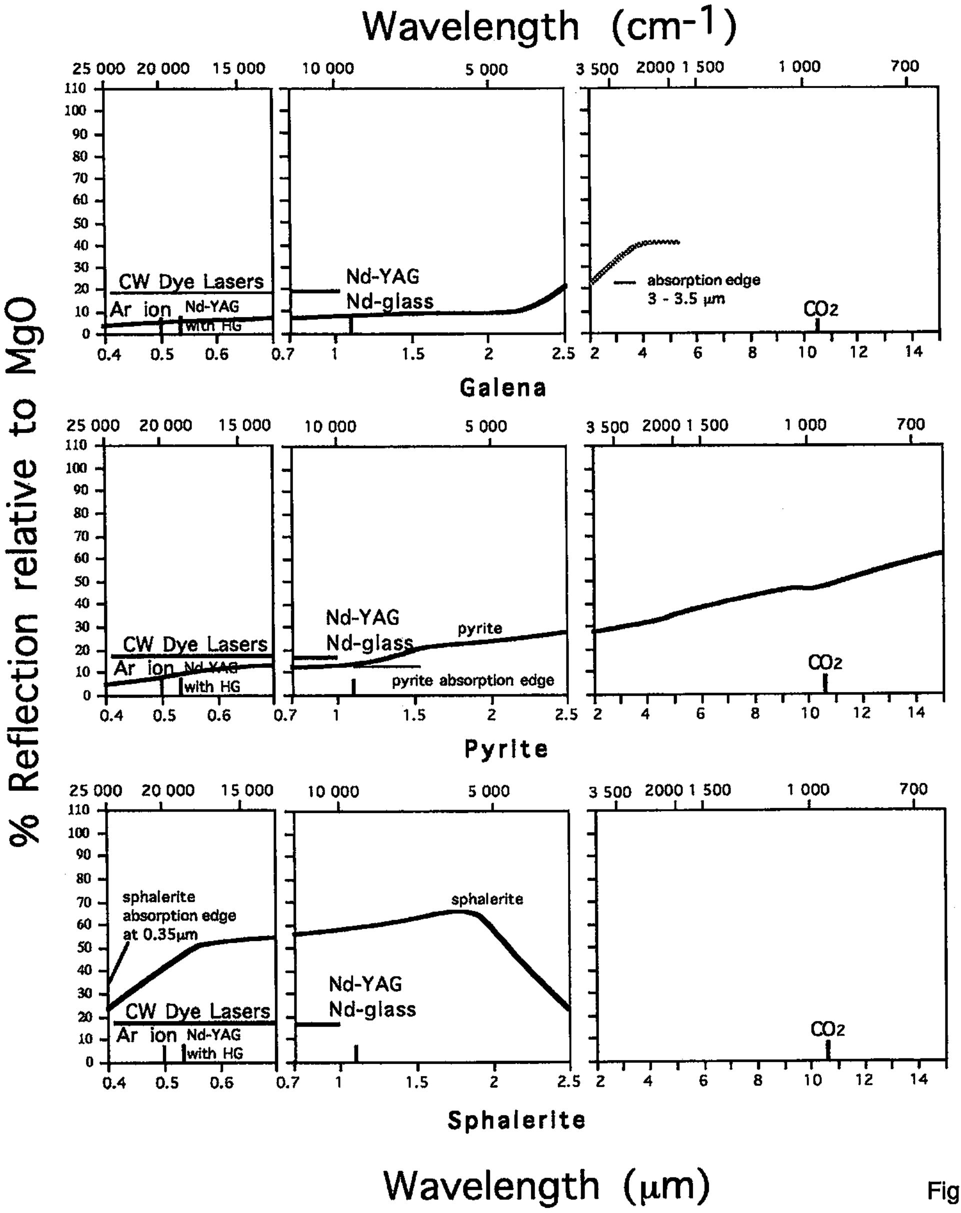

Figure 1d

FIG. 1. Reflectance of energy having wavelengths of 0.4–15 μm for quartz, orthoclase, albite, labradorite, garnet, biotite, olivine, pyroxene, calcite, dolomite, rhodochrosite, siderite, galena, pyrite and sphalerite relative to MgO. Also shown are the wavelengths of energy from CO_2, Nd:YAG, Nd-glass, Nd:YAG with half-grating (HG), Ar-ion and continuous-wavelength (CW) dye lasers, as well as the most probable effects on the absorption of each mineral. Compiled from data of Keller & Pickett (1949), Launer (1952), Huang & Kerr (1960), Milkey (1960), White & Roy (1964), Leise (1967), Hunt & Salisbury (1970, 1971), Omori (1970), and Hunt *et al.* (1971, 1973).

of absorption on UV laser-assisted analysis has yet to be examined. However, the absorption efficiency of UV energy by most minerals is relatively high, and thus is much less dependent on chemical composition than is the absorption of energy from Nd-type IR or CO_2 lasers.

Other lasers

Ar-ion lasers have wavelengths near 0.5 μm, and are absorbed to varying degrees by most silicates, sulfides and, to a lesser degree, carbonates (Fig. 1). These lasers are used extensively for Ar–Ar geochronology because of the small beam-diameter and the relatively high absorption-efficiency of most potassium-bearing silicates. Continuous-wavelength dye lasers have the advantage of relatively small beam-diameters and tunable wavelengths in the UV and visible ranges of the electromagnetic spectrum. Such lasers could be adjusted to maximize the absorption efficiency of specific minerals, thus minimizing the absorption effects of structural or chemical characteristics of samples. However, the cost of these lasers is prohibitive at present.

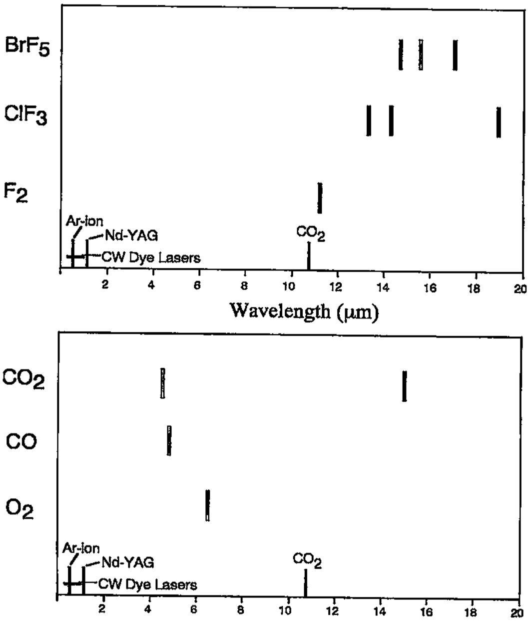

FIG. 2. Major absorption bands of reagents and gases produced during laser-assisted analysis of minerals, along with the principal wavelengths of various lasers. Data from Crawford *et al.* (1949), Rao (1950), Andrychuk (1951), Taylor *et al.* (1952), Claasen *et al.* (1958), and Begun *et al.* (1965).

The wavelength of the energy from a laser should not be absorbed either by reagents such as BrF_5, ClF_3, F_2 or O_2, used in the extraction, or gases such as CO_2, CO or O_2 released by the interaction of the laser beam and the sample. The major absorption bands of these gases do not correspond with the wavelengths of most lasers, although the energy from a CO_2 laser could be absorbed by F_2 and CO_2 (Fig. 2). Many of these reagents and reaction products can absorb UV radiation (*e.g.*, Wiechert & Hoefs 1993), which may severely limit the effectiveness of CO_2 and UV lasers.

Analysis of carbonate minerals

Most modern mass spectrometers can analyze less than 1 micromole of CO_2, which corresponds to about 0.1 mg of carbonate mineral. Conventional analysis requires that the samples be physically separated from their matrices and then dissolved in 100% H_3PO_4 to release the CO_2. The $\delta^{18}O$ values of the CO_2 must be corrected for fractionation effects due to the chemical composition of the carbonate, because the cations and one third of the oxygen from the original carbonate remain in the phosphoric acid solution (Sharma & Clayton 1965). Typical precision and accuracy for conventional analyses of small samples are ±0.1‰ for $\delta^{13}C$ and ±0.2‰ for $\delta^{18}O$. Computerized micro-drills (*e.g.*, Carpenter *et al.* 1991) are capable of removing specific phases with a spatial resolution of *ca.* 50 μm. This resolution is better than any of the laser-assisted systems described to date.

The first laser-assisted analysis of carbonates was reported by Smalley *et al.* (1989), who used a Nd:YAG laser to extract CO_2 from slabs of calcite having variable Fe content. Corrections for fractionation effects were estimated using pressed pellets of pure calcite and pure aragonite powders, the isotopic compositions of which were known from conventional analyses. The precision of this laser-assisted analysis was reported to be ±0.5‰ for both carbon and oxygen, on the basis of results from the pelletized standards. Subsequent publications by this group (Dickson *et al.* 1990, Smalley *et al.* 1992) used this same correction procedure for *in situ* analyses, although the corrections are slightly different for each study. Nd:YAG energy is absorbed primarily by transition metals, in particular Fe, so that the corrections estimated using pelletized calcite may not be appropriate for carbonates having different Fe contents. In addition, pelletization induces a great number of defects, cleavage and fracture faces, which both refract and enhance absorption of the laser energy to a much greater extent than coarser single-crystal samples. These effects may also influence the isotopic fractionation associated with the interactions between the laser beam and chemically complex carbonates.

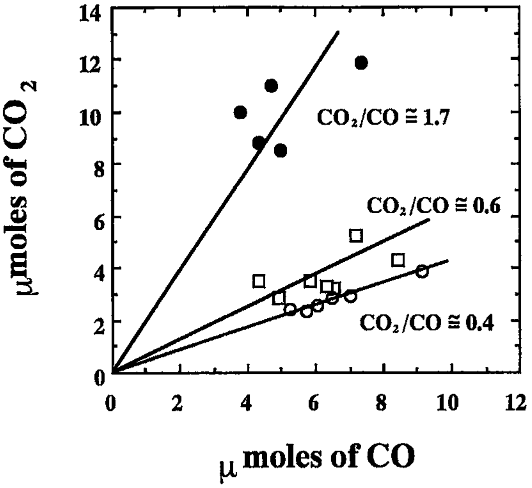

FIG. 3. Quantities of CO_2 and CO produced during laser ionization of various carbonate minerals using a Nd:YAG laser in continuous mode. Also shown are the CO_2/CO ratios for calcite (○), dolomite (□) and rhodochrosite (●). The number of laser pulses required to produce these data for calcite, dolomite and rhodochrosite was 200, 1500 and 50, respectively. Data from Powell & Kyser (1991).

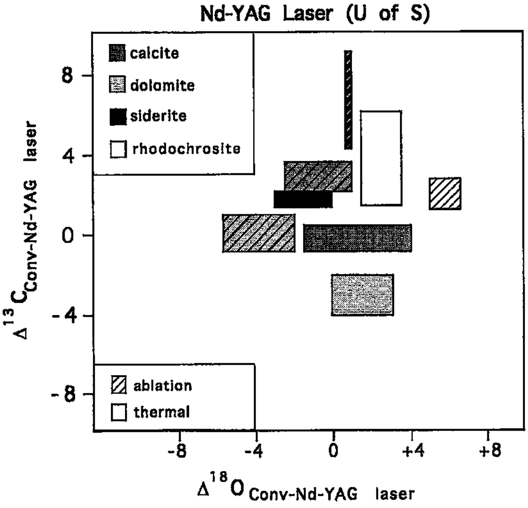

FIG. 4. Differences in the $\delta^{13}C$ and $\delta^{18}O$ values between conventional analysis (Conv) and analyses using a Nd:YAG laser for various carbonates. Hatched regions represent analysis where the carbonate was ablated by the laser's energy, and solid regions are data from analysis where the focal point of the laser was within the sample so that the carbonate was actually heated. Data from Powell & Kyser (1991) and subsequent analyses at the University of Saskatchewan.

In a detailed study of the processes involved in laser-assisted extraction of CO_2 from carbonates, Powell & Kyser (1991) showed that the yield of CO_2, the CO_2/CO ratio (Fig. 3) and isotopic fractionation (Fig. 4) associated with extraction of these gases from various carbonates using a Nd:YAG laser are very dependent on the chemical composition of the carbonate mineral. Furthermore, in marked contrast to what was apparently observed by Smalley *et al.* (1989), the data of Powell & Kyser (1991) from carbonates, Fallick *et al.* (1992) from sulfides, and subsequent data from studies at the University of Saskatchewan, indicate that polishing the sample, varying the energy and mode of the laser, and changing the focal point of the laser beam can all have substantial effects on the results (Fig. 4); this is as would be expected if the energy of the laser is not readily absorbed primarily by the groups of complex anions. Powell & Kyser (1991) also reported that a CO_2 laser, which heats the sample rather than ablate it (as can the energy from Nd:YAG lasers), resulted in more efficient extraction of CO-dominated gas from carbonates. However, isotopic fractionation produced by fixation of oxygen in the resultant oxide and volatilization of the carbonate at different temperatures along the reaction front are still a problem with the CO_2 laser. The isotopic compositions derived by *in situ* analysis using the CO_2 laser were found to be closer to those obtained by conventional analysis than to those using a Nd:YAG laser (Fig. 5), even though the precision from both laser systems is similar. Sharp (1992) reported limited success for *in situ* analysis of carbonates using a CO_2 laser, although the precision of the results was several times that of conventional analyses (Fig. 5).

Precise and accurate *in situ* analysis of the isotopic composition of carbonates would greatly benefit the earth sciences because most carbonate rocks contain several distinct generations of carbonate minerals, from which paleoenvironmental information could be obtained. At present, both the accuracy and precision of laser-assisted analysis have not approached those of conventional analyses, nor is the spatial resolution using a laser better than that obtained from microdrills. CO_2 lasers seem to provide more accurate *in situ* analysis of carbonates (*i.e.*, ± >0.5‰) than do Nd:YAG lasers, but the spatial resolution is typically 100–200 µm. Nd:YAG lasers have greater spatial resolution, but the fractionation effects are so dependent on the composition of the sample that very detailed chemical information about the sample and analysis of chemically equivalent standards must be available to obtain a precision better than ±0.5‰. Although laser-assisted analysis of carbonate minerals may be adequate for some studies, detailed paleoenvironmental studies and investigations aimed at tracing the isotopic evolution of seawater require greater accuracy and precision than can currently be provided with existing laser systems.

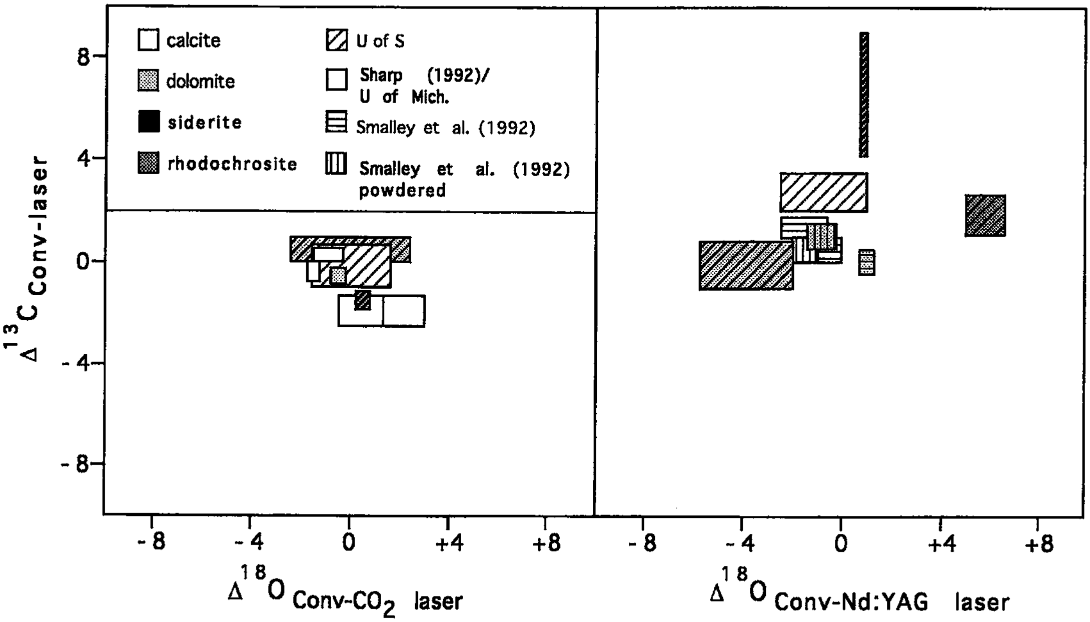

FIG. 5. Differences in the $\delta^{13}C$ and $\delta^{18}O$ values between conventional analysis (Conv) and analyses using a CO_2 laser (Sharp 1992, Univ. of Michigan) and Nd:YAG laser (Smalley *et al.* 1992, Univ. of Saskatchewan) for various carbonates. Only the data of Smalley *et al.* (1992) have been corrected using analyses on standards.

Analysis of silicate and oxide minerals

Laser-assisted analysis of the stable-isotope composition of silicates and oxides was pioneered by Franchi *et al.* (1986) and refined by Sharp (1990). Successful analysis of mineral separates by Sharp (1990) involved the use of a 20 W CO_2 laser impinging on a sample in a reaction chamber with a partial pressure of either BrF_5 or ClF_3. The oxygen released by this reaction is passed through a hot mercury trap to remove any fluorine and then converted to CO_2 by reaction with hot graphite; the CO_2 is then admitted on-line to an isotope-ratio mass spectrometer. Sharp (1990) reported that the precision and accuracy of this extraction system approach those of conventional techniques for some minerals (Fig. 6), which is not surprising given

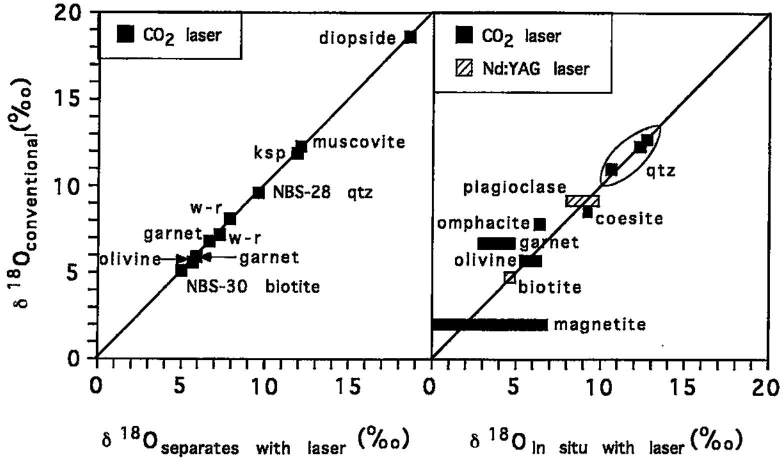

FIG. 6. Comparison of $\delta^{18}O$ values obtained from conventional fluorination with $\delta^{18}O$ values obtained using a CO_2 laser system on mineral separates and CO_2 and Nd:YAG lasers for minerals analyzed *in situ*. Data from Sharp (1990, 1992), Elsenheimer & Valley (1992), and Mattey & Macpherson (1993).

that both techniques are identical except that one uses a laser rather than a resistance heater to cause the reaction between the sample and the fluorinating agent. Sharp (1990) also reported results from *in situ* spot-analysis of quartz, magnetite and olivine, with values of accuracy and precision of ± several ‰ (Fig. 6).

A purportedly high-precision laser-assisted extraction line for ferromagnesian minerals has been described by Mattey & Macpherson (1993). The system uses a 60 W continuous Nd:YAG laser to react olivine, pyroxene and garnet separates with ClF_3. As with all other laser systems, a residue, presumably of fluorides (*e.g.*, MgF_2, CaF_2, *etc.*), remains after the reaction is complete. Although the system is capable of producing $\delta^{18}O$ values on samples of *ca.* 1 mg, the accuracy and precision for small samples are severely limited by two aspects, namely difficulties in converting small amounts of O_2 to CO_2 and the necessity of obtaining 100% yield (Fig. 7a). Despite assertions that this system is more accurate for analysis of refractory phases than are conventional systems because yields of 100% can be obtained, any yield less than 100% using this system produces an incorrect $\delta^{18}O$ value (Fig. 7b).

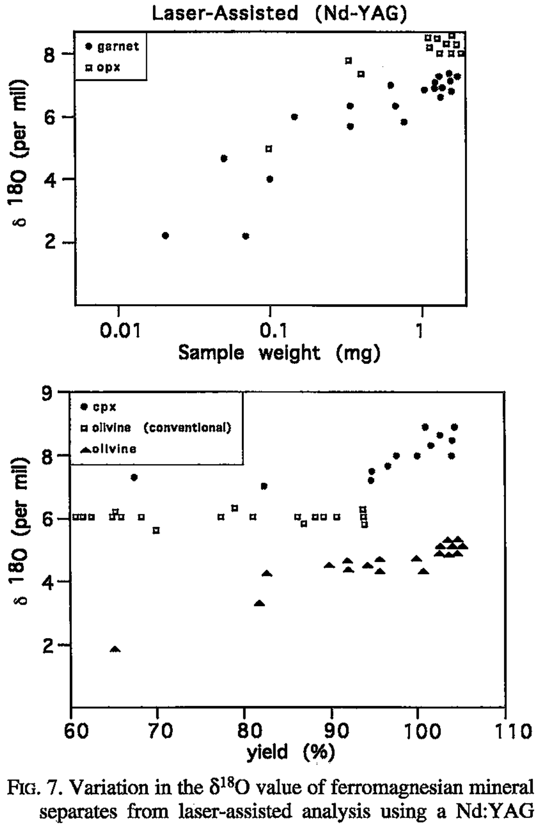

FIG. 7. Variation in the $\delta^{18}O$ value of ferromagnesian mineral separates from laser-assisted analysis using a Nd:YAG laser and conventional analysis as a function of sample weight and percent yield of O_2. Data from Mattey & Macpherson (1993), Kyser *et al.* (1981) and this study.

This system as described cannot assure that yields are always 100% because of the large errors associated with accurately weighing small samples and uncertainties in knowing what the yield should be because of variations in the chemical composition of natural minerals. In contrast, the accuracy of conventional analysis of these minerals is not dependent on yield (Fig. 7b). The high precision claimed by the authors is only valid for some samples, and analysis of most samples, and all standards, reported by Mattey & Macpherson (1993) have a reproducibility in excess of ±0.3‰. Moreover, analysis of samples with low Fe contents with this system is difficult because the energy from a Nd:YAG laser is not efficiently absorbed.

Mattey *et al.* (1993) used this system to analyze minerals in mantle xenoliths and reported that the $\delta^{18}O$ value of olivine in the mantle is consistently 5.2 ±0.2‰. This result is in direct conflict with those obtained in several other studies of both mantle-derived olivine and silicate liquids, both of which range between 4.5 and 7.0‰ (Kyser *et al.* 1981, Harmon *et al.* 1986, Kempton *et al.* 1988, Kyser 1990). More recently, Mattey *et al.* (1994) analyzed samples of mantle-derived minerals using the Nd:YAG laser system that were previously analyzed conventionally by Kyser (1990, unpubl. data). Conventional analyses of the olivine vary by 1.5‰, from 4.8 to 6.3‰, whereas laser-assisted analysis of the same olivine separates vary by only 0.4‰, from 4.9 to 5.3. Differences between the values using the two techniques vary as a function of the conventional $\delta^{18}O$ value; values from the techniques are identical for samples with conventional $\delta^{18}O$ values near 5.0, but differ markedly for samples with higher conventional $\delta^{18}O$ values. The accuracy and precision of the laser system for analysis of minerals such as olivine and the effect of chemical composition on these results have not been adequately tested. In addition, the small samples of *ca.* 1 mg, normally of high optical quality, used by Mattey *et al.* (1994) for laser analysis may not truly represent the average value of olivine in a mantle xenolith, whereas conventional analysis normally uses larger sizes of samples taken from several grams of powdered olivine from a xenolith. Clearly, more careful and thorough comparisons of results from laser and conventional analysis are required before any sweeping scientific conclusions about the mantle are made on the basis of results from a new, untested technique such as the Nd:YAG system.

The oxygen-isotope composition of submillimetric domains in quartz and feldspar separated from hydrothermally altered granite from the Isle of Skye was measured with a CO_2 laser system by Elsenheimer & Valley (1993). The authors concluded that variations in the $\delta^{18}O$ values of feldspar phenocrysts in the granite reflect extent of isotope exchange with infiltrating meteoric water at high temperatures. Both the accuracy and precision of the results are about ±0.5‰. The isotopic variations observed from fine-scale sampling of minerals are comparable to the variations in whole-rock samples of this granite reported by Forester & Taylor (1977).

Systems based on laser-assisted extraction can produce reliable isotopic measurements on some minerals in amounts smaller than many conventional systems. The true advantage of laser systems, however, lies in their *potential* for accurate and precise *in situ* analysis of silicates and oxides. Sharp (1992) analyzed several minerals *in situ* with a CO_2 laser and reported an accuracy of 0–3‰, and a precision of ±0.5‰, depending on the mineral analyzed (Fig. 6). Subsequently, similar accuracy and precision were reported for *in situ* analyses of feldspar and quartz in samples of anorthosite and granite by Elsenheimer & Valley (1992) using a Nd:YAG laser system, although the energy from this laser is normally not absorbed by these minerals. The results were used to argue that restricted ranges in the $\delta^{18}O$ values of plagioclase from the Marcy Anorthosite Massif indicate that the influence of later fluids was minimal, whereas variations in excess of 1‰ in the $\delta^{18}O$ values of quartz and plagioclase in granite from the Siljan Ring astrobleme, Sweden, indicate interaction with late fluids.

Most of the other studies with laser-assisted analysis employ a CO_2 laser to analyze the isotopic composition of silicates *in situ* (Sharp 1991, Conrad & Chamberlain 1992, Kirschner *et al.* 1993, Chamberlain & Conrad 1993, Young & Rumble 1993, Kohn *et al.* 1993). The authors of these studies used variations in the $\delta^{18}O$ values of coexisting metamorphic minerals such as quartz, garnet, staurolite, muscovite and chlorite to constrain the origin, temperature and flux of fluids associated with formation or recrystallization of these minerals. For example, Conrad & Chamberlain (1992) argued that variations of nearly 5‰ in hydrothermal quartz veins with the same temperatures of fluid-inclusion homogenization resulted from changes in the isotopic composition of the vein fluids. A similar result was obtained by Kirschner *et al.* (1993) using the laser-assisted extraction system described by Sharp (1990) on quartz veins in the Alps of central Austria. In systems where isotopic variations are several ‰, *in situ* analysis with a laser seems to give reasonable results.

Analysis of sulfide minerals

Crowe *et al.* (1990) described a system for *in situ* analysis of sulfide minerals using a Nd:YAG laser to heat the sample in the presence of O_2. The resulting SO_2 was collected, purified and analyzed with a precision of ±0.3–0.9‰. The accuracy of these results was found to be dependent on corrections that varied as a function of the chemical composition, assuming that the corrections for the oxygen isotopic composition of the SO_2 from the sample are identical to those in the standard. Detailed electron-microprobe and SEM examination of the resultant reaction-area in the sulfides clearly shows that a reaction front surrounds each crater created by the laser. The extent of the reaction front is different in each type of sulfide examined and contributes to the fractionation of sulfur isotopes, for which correction factors had to be applied. Fallick *et al.* (1992) suggested that the precision and accuracy of this analysis could be enhanced using an appropriate *modus operandi* that involves relatively low power.

Procedures similar to those of Crowe *et al.* (1990) were described by Kelley & Fallick (1990), who used an Ar-ion laser that also required correction factors for each sulfide mineral. An extraction system with improved precision was described by Beaudoin & Taylor (1993). In this system, SF_6 is made using a CO_2 laser to heat sulfides in the presence of F_2, thus eliminating any variations due to the isotopic composition of oxygen. As with many other laser-extraction systems, the effects of variable chemical compositions of sulfide minerals on accuracy and precision have yet to be evaluated in detail.

Analyses of hydrous minerals

Laser-assisted analysis of the hydrogen-isotope composition of minerals poses additional problems to those encountered in the analysis of other isotope compositions. Not only can the fractionation of hydrogen isotopes be significant during extraction of hydrogen gas or water from a mineral using a laser, but the surfaces of most natural substances are replete with layers of absorbed water that dilute the hydrogen released from the structure. This surface-adsorbed H_2O is extremely difficult to remove and significantly affects micro-analytical results, not only for laser-assisted systems, but also for SIMS analysis (Deloule *et al.* 1991).

The laser-extraction system at the University of Saskatchewan uses a Nd:YAG laser with a wavelength of 1.064 μm that impinges on a sample in a heated chamber. Any H_2 released during interaction of the laser energy with the mineral (usually 10–20 mol% of the H_2O released) is converted to H_2O *via* reaction with CuO, and this water is cryogenically collected along with any H_2O released, purified, converted to H_2 gas with hot uranium metal and admitted directly into a MAT 251 isotope-ratio mass spectrometer. Sample sizes as small as 3 micromoles produce accurate results for samples of standard H_2O with this system, with a precision of ±7‰. Samples of phlogopite, biotite, amphibole, muscovite, serpentine and kaolinite were analyzed *in situ* using polished slabs. In addition, the H_2O in carnallite and fluid inclusions in halite also were extracted with this system.

The δD value decreases dramatically with increasing yield of H_2O for all hydrous minerals (Fig. 8). Collectively, the data for all minerals analyzed indicate mixing from two reservoirs, one having a relatively

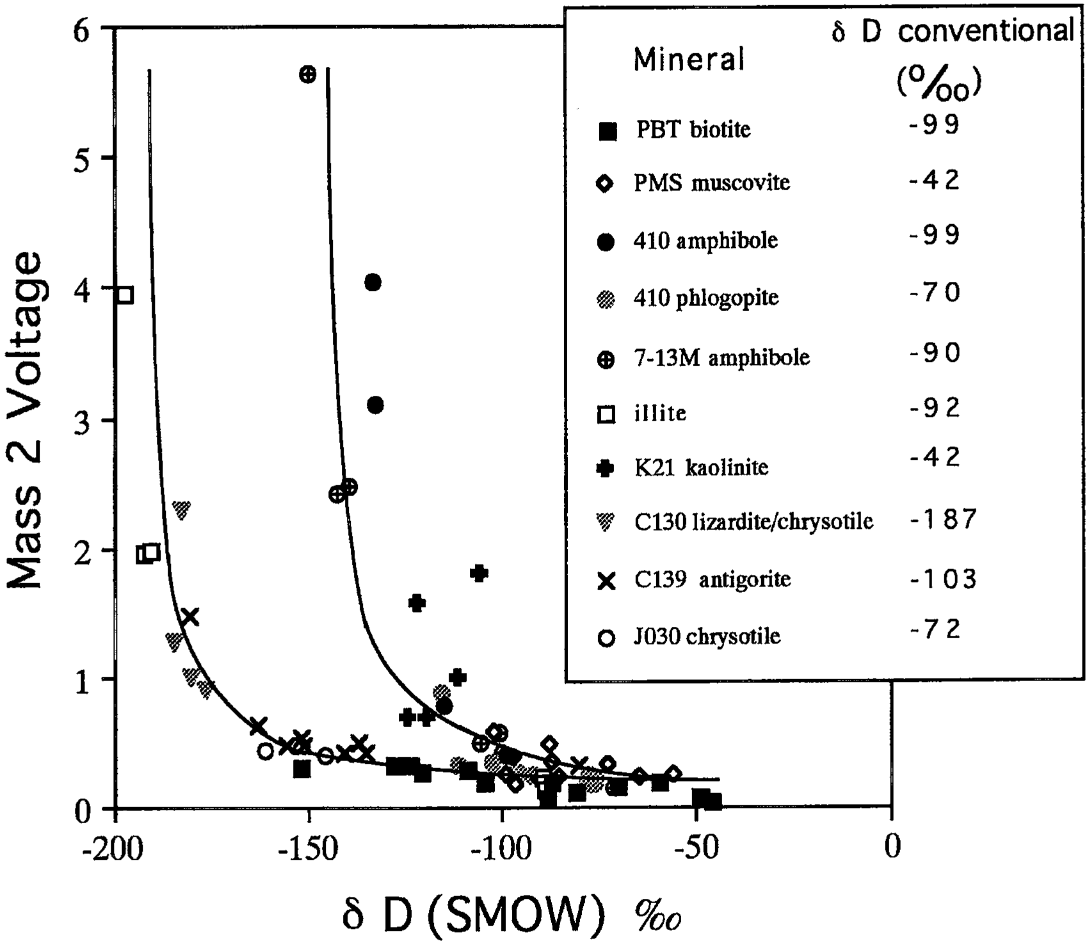

FIG. 8. Relation between the intensity (voltage) of mass 2, which corresponds to the amount of H_2 obtained, and the δD value for hydrous minerals analyzed *in situ* using a Nd:YAG laser system. Also shown are the values obtained from conventional analysis.

high δD value near that obtained from conventional analysis of each mineral, and the other having a low δD value of *ca.* –180‰ (Fig. 8). Moreover, the yield of H_2O decreases, but the δD value increases, for most samples during their residence in the vacuum system (Fig. 9). These results are compatible with the interpretation that D-depleted surface-adsorbed H_2O contributes substantially, but variably, to the H_2O released from each mineral. Further evidence exists that adsorbed H_2O contributes to the hydrogen extracted from *in situ* laser-assisted analysis: the δD value of water vapor in the laboratory is near –200‰. Moreover, olivine and pyroxene separates heated in the vacuum chamber for several days not only have significant contents of water (*ca.* 0.2 wt%), but also δD values near –200‰, presumably because of adsorbed H_2O on the surface of the grains. Despite heating the sample in vacuum for several days and heating the surface of the slab using an unfocused laser beam, the adsorbed H_2O could be minimized but not eliminated. However, not all of the difficulties in this type of analysis are due to adsorbed H_2O; even when the effect of adsorbed H_2O is reduced, aberrant values were still obtained. Apparently, the light isotopes of hydrogen are preferentially released during reaction of hydrous minerals with the laser beam because small fragments resulting from the interaction of the laser with the mineral, and the area of the mineral immediately surrounding the melted or ablated region, have δD values greater than those obtained from conventional analysis. This effect varies for each mineral, as would be expected, because the absorption efficiency of Nd:YAG energy varies with Fe content. Unless the adsorbed H_2O can be eliminated and the laser energy

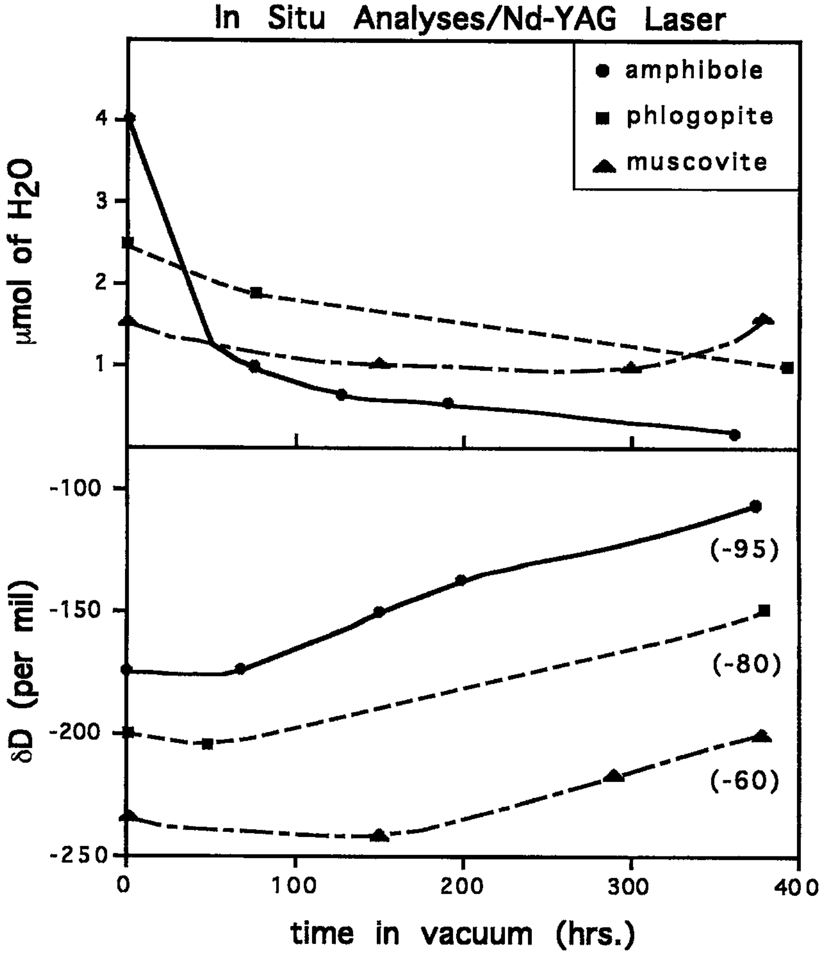

FIG. 9. Changes in the quantity of H_2O released (in µmoles) and δD value with time spent by the sample in a heated vacuum chamber prior to analysis. A Nd:YAG laser was used to extract the H_2O from the hydrous minerals. The δD value of each, as derived from conventional analysis, is shown in parentheses.

has a sharp reaction-front (as may be the case if UV lasers are used), it is unlikely that laser-assisted hydrogen-isotope analysis will produce accurate results for *in situ* analysis of minerals.

Model for in situ laser-assisted analyses

All studies that have used a laser to analyze samples *in situ* indicate that the energy from the laser is absorbed differentially depending on the structure, composition and crystallinity of the sample. In every publication to date involving laser-assisted analysis for either isotopic or chemical (ICP–MS) composition, SEM and back-scatter photomicrographs show that the area around the reaction pit made by the laser beam is also affected by the laser energy, and likely contributes to isotopic and chemical fractionation. The absorption spectra of minerals indicate that UV energy is more efficiently absorbed than energy in the visible or IR range of the spectrum (Fig. 1), and researchers working on laser-assisted ICP–MS analysis have capitalized on this. However, not all minerals will absorb UV laser energy in the same way, and the small, but perhaps important, effects of chemical composition, structure, defect density, and presence of fluid inclusions on the absorption efficiency of natural materials for any laser have yet to be studied in any detail.

A general model for the interaction between a laser beam and a sample is shown in Figure 10. The energy from the laser beam is absorbed differentially, depend-

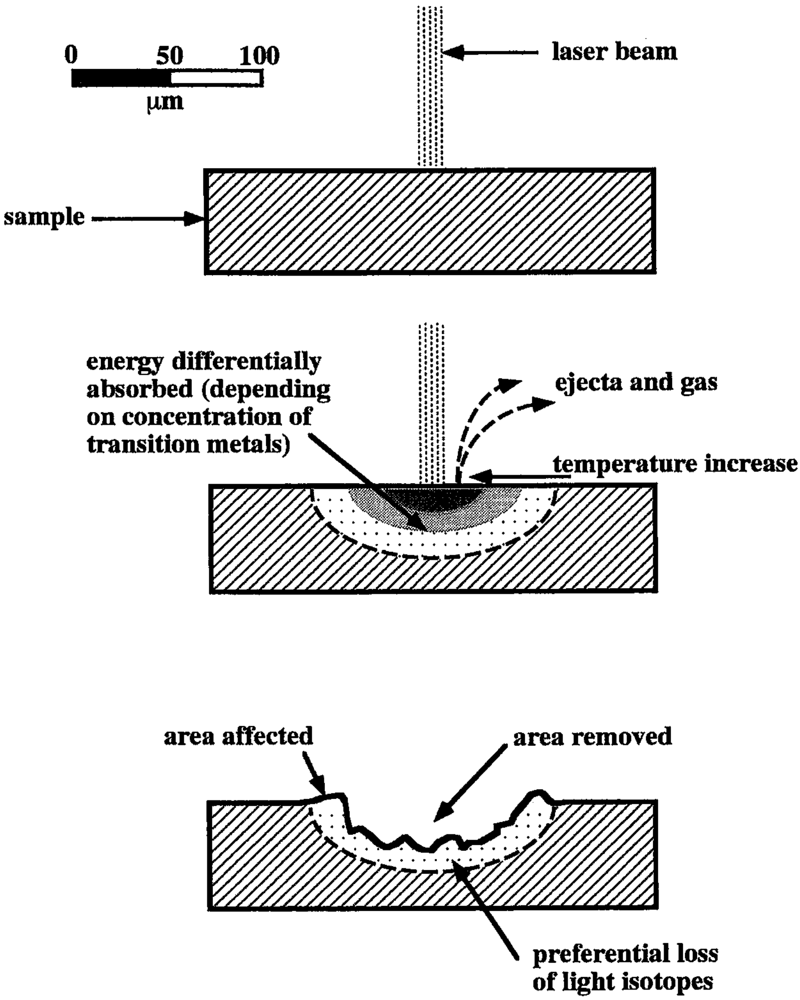

FIG. 10. Generalized model for the interaction of laser energy with a sample. The laser energy would be absorbed differentially depending on chemical composition, structure, defect density and the type of laser used, thus resulting in a temperature gradient around the area where the laser beam impinges on the sample. Depending on the steepness of this gradient, a significant area beyond that obviously removed by the laser may be affected, resulting in the preferential loss of light isotopes.

ing on such factors as crystallographic orientation, defect density, presence of inclusions and chemical composition. A temperature gradient will exist depending on how the energy is absorbed, and the character of the ejecta and gas liberated from the surface of the sample will be a function of the local temperature. Furthermore, condensation will enhance isotopic and chemical fractionation, as will the temperature gradient. Therefore, the area of the sample affected by the laser energy will be greater than the area removed, especially if the temperature gradient is not infinitely steep.

STABLE-ISOTOPE ANALYSIS WITH SIMS

In situ analysis of minerals using secondary-ion mass spectroscopy (SIMS) has the advantage over laser-assisted analysis of excellent spatial resolution, but at the expense of reduced accuracy and precision. The hydrogen-isotope composition of micas and amphiboles in mantle xenoliths has been determined using SIMS (Deloule *et al.* 1991, Kinny *et al.* 1993). The δD values vary with degree of metasomatism. *In situ* analysis of the hydrogen-isotope compositions of phases in meteorites by Deloule & Robert (1993) indicate that interstellar δD values vary from –600 to +5000‰. Similar to the problems encountered with laser-assisted *in situ* analysis of hydrous minerals discussed above, the ion-microprobe results also are subject to problems as a result of adsorbed H_2O (Deloule *et al.* 1991).

Boron, O, C and S isotopic compositions of minerals determined by SIMS have a precision of ±2‰ at best. Despite this relatively low precision, SIMS data have been used to determine the origin of authigenic overgrowths on detrital quartz (Arbey *et al.* 1993), zoning of oxygen isotopes in metamorphic minerals (Valley & Graham 1993) and the variation in the $\delta^{34}S$ values of mantle-derived sulfide minerals (Chaussidon *et al.* 1989). The substantial variations in the $\delta^{34}S$ values in sedimentary sulfides, sulfides from Mississippi-Valley-type deposits and zoning in sulfides from hydrothermal systems observed on the macroscopic scale using conventional analysis have been studied in detail on the micro scale using SIMS (McKibben & Eldridge 1989, Cole *et al.* 1993, Eldridge & McKibben 1993). The greatest potential of SIMS may be in constraining the amount of time and the temperature at which two minerals have been in contact with one another (*e.g.*, Valley & Graham 1991), provided the variations in isotope ratios are significant.

SYNOPSIS

Novel micro-analytical techniques such as SIMS, laser probe and new conventional techniques can be used to examine the presence of equilibrium, and consequences of kinetic effects in natural systems. SIMS has excellent spatial resolution for *in situ* analysis, but lacks the necessary precision of *ca.* a few tenths of a permil required by most studies. The accuracy and precision of laser-assisted analysis may be far more dependent on the chemical and physical characteristics of minerals than was first realized, especially in the case of *in situ* analysis; these effects may be minimized with appropriate choice of laser once more thorough studies are complete. Conventional techniques are, and probably will, continue to be the mainstay of isotope analysis because of their unrivaled accuracy and precision. Each of these techniques has advantages and disadvantages over the others, and all of them must be used with circumspection. The tendency of many researchers is to assign significance to data obtained with new techniques prior to a critical examination of the possible deficiencies of these techniques. This has been a lesson learned over a great period of time by electron-microprobe analysts, and one that should not be forgotten in developing new micro-analytical techniques for isotopic determination. As the techniques described above are refined, others on the horizon, such as laser-resonance spectroscopy, which measures the isotopic composition of specific phases in complex mixtures (*e.g.*, Murnick & Peer 1994), are being explored, hopefully with the appropriate rigor.

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