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ULTRASENSITIVE TRACE-ELEMENT ANALYSIS WITH ACCELERATOR MASS SPECTROMETRY: THE CURRENT STATE OF THE ART

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ABSTRACT

Accelerator Mass Spectrometry (AMS) is a variety of SIMS that uses high (MeV) energies to ensure the total removal of molecular ions from a beam of secondary negative ions generated from a small ($\sim 10^6$ μm^3) volume of sample material. AMS has been used for ppb-level measurements of concentrations of precious metals in individual grains of conductive minerals. With a strictly zero background level, the detection limits and spatial resolution depend on ion-source constraints, negative secondary-ion formation, charge changing, mass spectrometry and detection efficiency; generally speaking, 1 atom out of 10^5 sampled identical atoms will be detected. In the range of microbeam analytical methods, AMS has the best levels of detection (<<1 ppb), but the poorest spatial resolution; this latter limitation arises mainly from the use of traditional ion-source design that is commensurate with radiocarbon dating.

Keywords: accelerator mass spectrometry, noble metals, analysis for precious metals, SIMS, negative ions, ultrasensitive analysis, trace elements.

SOMMAIRE

La spectrométrie de masse avec accélération est une variété de la technique de spectrométrie de masse des ions secondaires qui utilise une énergie élevée pour assurer l'élimination complète des ions moléculaires d'un faisceau d'ions négatifs secondaires produits dans un volume restreint ($\sim 10^6$ μm^3) de matériau. Cette technique a été utilisée pour obtenir des mesures de concentrations de métaux précieux inférieures au ppb dans des cristaux individuels de minéraux conducteurs. Avec un bruit de fond strictement égal à zéro, les limites de détection et la résolution spatiale dépendent des contraintes dues à la source des ions, à la formation des ions secondaires négatifs, au changement des charges, à la spectrométrie de masse et à l'efficacité des détecteurs. En général, un atome sur 10^5 atomes négatifs échantillonnés sera décelé. Parmi les méthodes analytiques fondées sur l'utilisation de microfaisceaux, la spectrométrie de masse avec accéleration peut offrir les seuils de détection les plus faibles (<<1 ppb); par contre, la résolution spatiale est la plus faible. Cette limitation serait surtout la conséquence de l'utilisation d'une configuration traditionnelle de la source des ions, conçue pour la datation par radiocarbone.

(Traduit par la Rédaction)

Mots-clés: spectrométrie de masse avec accéleration, métaux nobles, analyse pour teneurs en métaux précieux, spectrométrie de masse sur ions secondaires, ions négatifs, analyse ultrasensible, éléments traces.

INTRODUCTION

Accelerator mass spectrometry (AMS) has become the main method to analyze for rare long-lived radionuclides, such as ^{10}Be, ^{14}C and ^{129}I, which occur naturally; ratios relative to their major stable isotope ($^{10}Be/^{9}Be$, $^{14}C/^{12}C$, $^{129}I/^{127}I$) are less or equal to 10^{-12}. Although there are procedural variations between laboratories, the requisite technology is now mature (Litherland 1984, 1990), and applications span such fields as Quaternary geology, oceanography and archeology. Despite major advances, research and development of AMS for ultrasensitive (<1 ppb) analysis for trace elements has progressed more slowly.

This note describes facets of sampling and analysis pertinent to current and projected AMS services in the area of measuring concentrations of trace elements and isotope ratios. The intention is not to review individual case-histories or repeat published data. For an overview of the method's application to precious metals in ore minerals, its intimate relationship to keV-energy Secondary Ion Mass Spectrometry (SIMS), aspects of quantification and standardization, and additional references, see Wilson *et al.* (1991, 1995). Related applications to minerals, meteorites and impact rocks are described by Chew *et al.* (1984), Fehn *et al.* (1986) and Rasmussen *et al.* (1989).

CONCENTRATIONS OF TRACE ELEMENTS BY AMS: A RATIONALE

There are many parameters to judge the worth of a method of geochemical analysis. Beyond such "givens" as reproducibility and linearity in standardization, individual scientists may place particular emphasis on one or more options, ten of which are listed below: (a) Intrinsic factors: accuracy, precision, sensitivity; (b) Logistics: accessibility, cost, throughput; (c) *In situ* analysis: chemical bonding, depth profiling, sample stability, spatial resolution.

A major problem with AMS is access to equipment. Virtually all AMS data on precious metals have been collected at three laboratories: Oxford, Rochester and Toronto. Apart from restricted availability of suitable AMS facilities, discussions with current and potential users indicate that wider use of AMS in geological trace-element work would best be promoted by the adoption of finer, variable-width primary-ion beams (ideally, ≈30–1000 μm) in AMS labs; 200 - 1000 μm has been the typical beam-size used. The only other use of AMS for trace-element measurement has been in relation to the determination of impurity levels in semiconductor materials (Anthony *et al.* 1985, 1991), where the emphasis has been on multielement analysis capability, comparable to that achieved for the rare-earth elements by SIMS (Shimizu 1992) or laser-ablation ICP–MS (Jackson *et al.* 1992).

The analysis of geological samples for precious metals by AMS has now been developed and used in some 45 papers, abstracts and theses. It seems clear that a second generation of projects is in order, to advance analytical techniques both for precious metals and for a wider range of trace elements. The larger volume sampled (not an intrinsic characteristic of AMS, merely of the ion sources commonly used) and higher sensitivity of AMS (partly a reflection of sample volume, but also a product of the highly ion-specific, zero-background nature of AMS) place it at one end of a continuum of *in situ* analytical tools. From smallest-sample, highest level of detection to largest-sample, lowest level of detection, these comprise electron, proton and ion microprobes, and AMS. As discussed below, the unique advantages of AMS lie in its extremely high sensitivity and freedom from background, and in the diversity of options for selection (at keV energies) of secondary ions from a sample, followed by complete isolation of the required (MeV) ions from interfering species.

SAMPLE PREPARATION

Application of new techniques, such as X-ray diffraction and the electron microprobe, to ever-smaller samples accounts for the rapid rise in the number of new mineral species described since the 1920s (Skinner & Skinner 1980). The success of interpretations based on SIMS data for small samples (hand specimens, or smaller) in explaining aspects of much larger (mine-scale to regional) geological features was reviewed by Eldridge *et al.* (1989). In common with all other laboratory studies that extrapolate from the very small to the very large, care must be taken to integrate AMS data properly within a wider context of field and laboratory observations, in order to avoid erroneous interpretations.

In the trace-element context, AMS has been applied to both polished surfaces of minerals and pressed, powdered samples of rock (Rucklidge *et al.* 1990, 1992). Most of the samples were analyzed as polished cores in sets of 12, preserving spatial information on a scale of around 1 mm. In each case, samples were subjected to careful microscopic examination, and in some cases electron-microprobe analysis, prior to sampling for AMS work. Despite the very different volumes sampled, these techniques are complementary, AMS providing compositional data below the detection limit of the electron microprobe (typically a few hundred ppm). In the case of pressed powder samples, the chosen reference material and the unknowns are mechanically mixed (50:50 volume proportions) with a powdered graphite medium, in order to ensure electrical conductivity and provide a common matrix for the measurements.

Recent analysis of drilled, polished cores of sulfide and oxide ores and of natural and synthetic samples of graphite, copper and sulfides at IsoTrace has used polished targets mounted with appropriate standard reference materials and mass-calibration targets in composite mounts. The mounts, 25 mm in diameter, are machined from aluminum, and each houses 12 targets. The key to this method of sample preparation lies in the conducting, vacuum-compatible mounting medium devised for AMS use at IsoTrace.

A "secondary sampling" occurs on the sample stage, where a probing beam of primary ions sputters and ionizes the target. Liebl (1975a, b) reviewed intrinsic limitations due to minimum size of sample necessary to detect a certain concentration of an element (or a minimum number of atoms), coupled with factors of primary-beam current, ion yield and erosion rates of samples. His work was directed toward SIMS, but the general principles also apply to other *in situ* methods.

For individual grains of a mineral, AMS has been shown to work reliably only on those materials that are electrically conducting, such as sulfides and certain oxides (*e.g.*, magnetite, hematite). Nonconducting grains (*e.g.*, silicates) require a mechanism of surface-charge compensation such as electron flooding or continuous cesiation of the surface, cesium atoms being deposited on the sample surface, providing a metallic coat. This is technically feasible (Freeman 1992, Freeman *et al.* 1993), but has not yet been applied routinely to AMS measurements.

THREE STRATEGIES FOR VERSATILITY IN ULTRASENSITIVE ANALYSIS

Sampling size

This factor involves more than simple access to ever-smaller target grains. On one hand, it represents a trade-off between sensitivity and spatial resolution, with both the cross-section and sampling depth of each analysis at stake.

The sampling volume used in various techniques varies by orders of magnitude. Thus for an electron microprobe using 20 keV electrons, penetration into mineral targets such as copper, pyrite and quartz may be only 1 – 1.5 μm. The volume of X-ray excitation for an electron beam 3 μm in diameter is ≤10 μm^3. In comparison, PIXE (where the MeV protons have much longer ranges in the target) and SIMS (where the surface is progressively sputtered away) may sample thousands of μm^3. Similar volumes may be attained with Synchrotron X-ray Fluorescence (SXRF), which can be used to determine the concentration of PGE and other trace elements (*e.g.*, Smith *et al.* 1987, Saito *et al.* 1993), and may, as is true for AMS and SIMS, make an optimal contribution when combined with other techniques (*e.g.*, Kucha *et al.* 1993). However, with the exception of SIMS, none of these methods approach sensitivities better than the ppm level. In AMS, with beam sizes presently in the range 300–1000 μm, an aggregate 3000-second, eight-element sequence of precious-metals measurements in high-current mode might produce a saucer-shaped crater in sulfide, 1 mm in diameter. Continuing this approximation, some 2×10^5 μm^3 of sample would be eroded in 10 seconds, the typical time for analysis of samples for gold or silver. This volume corresponds to approximately 1 – 1.5 μg of common sulfides, and 2 μg of native copper. Predictably, the sampling volume and the detection level (lower limit for reliable detection of a species) are both a function of sampling time. The sampling volume is approximately five orders of magnitude more than that sampled by an electron beam, two orders of magnitude more than PIXE or SIMS (as described by Cabri *et al.* 1991), but is still five orders of magnitude less than small aliquots commonly used in bulk analysis by INAA, and still preserves spatial chemical information.

There is no physical barrier to obtaining smaller primary-ion beams for AMS. Ideally, the ability to vary the beam diameter and current within wide limits would satisfy alternate priorities for small targets or very low concentrations of analyte. The ability to minimize the rate of erosion also would permit the option of ion implantation for matrix-effect control and standardization, currently impractical with the "radiocarbon" style of high-current ion source.

With a typical observed count-rate of ~3 counts/s/ppb Au^{6+} on a standard sulfide bead containing 470 ppb gold, the implication is that some 14,000 ions are detected in 10 seconds from a sampled volume that should contain $\sim 1.3 \times 10^9$ atoms of gold. This suggests that only 1 atom in 10^5 within the sample is (1) sputtered from the sample, (2) forms a monatomic negative ion within the effective field of extraction of the ion source, (3) traverses the spectrometers with a trajectory accepted by all the analyzing elements (including slits), while (4) undergoing the appropriate charge-changing collisions in the terminal of the accelerator, in order to (5) be detected by a solid-state or gaseous ionization detector. As a first approximation, the detector may be ruled out as a major source of this inefficiency. The observation may be ascribed to three compound losses in processes with ~1% efficiency: (1) monatomic ion formation; (2) charge-changing to the commonly selected q = 6+ ion at a terminal energy of ~2 MeV; (3) overall geometrical transmission through the instrument in which the path length of the beam is approximately 25 m. Given quoted limits of detection for other analytical methods, similar or greater losses must occur for these too, if not in signal generation (sputtering, or its equivalent mechanism of excitation), then in "dark current" or interference-related backgrounds at the detection stage. The "dark current" is the detector signal measured in low-energy ion detectors when there is no beam reaching the detector; this is strictly zero in the high-energy detectors used in AMS. The inefficiency of charge-changing is the price paid by AMS for its normally zero losses in background.

Throughput

A complex system such as an AMS facility can only compete with simpler techniques by (1) high efficiency, (2) some unique attribute, such as unparalleled sensitivity at a given sample size (as in ^{14}C measurements), or (3) where there are no alternative techniques.

It is clear that a wide range of methods are quickly becoming automated to the point where rapid multi-element scans can be achieved at ppm levels. Techniques such as SIMS, PIXE and laser-ablation ICP–MS come to mind. With prolonged count-times, or repeated sampling of the same target, these may also be capable of smaller throughput of lower-level analyses, in some cases down to the ppb level. We argue elsewhere in this note that the versatility of AMS as a analytical tool for materials science is its paramount importance. Nonetheless, can existing systems be made more efficient? Several developments at IsoTrace aim at increased efficiency. At the ion source, a new dual ion source with an enlarged, computer-controlled stage has been built and is in the process of installation. With a sample area of ~6 × 9 cm, the option of sequential analysis of 60 or more targets (or even more points within suitable large, polished samples) on tractable elements (Au, Ag, Pt, and other good producers of negative ions) within an hour at ppb levels or below will be achieved. Computer control of the analyzing magnets with peak-switching software could enable automatic (sequential) analysis of such samples for several elements, instead of a single element as at present. Continuous cesiation of insulating surfaces would also allow silicate targets to be analyzed.

Analytical strategy

The most appealing aspect of AMS for ultrasensitive mass spectrometry is its great versatility. The complexity of analytical elements (electric and magnetic sectors, electron-stripping components and diverse detectors), which poses a significant challenge to precise and rapid peak-switching over wide ranges of mass, also confers some unique benefits. The large analyzers, capable of bending MeV-energy heavy ions, allow a choice of charge states, avoiding mass-charge ambiguities in a manner unavailable to keV techniques (Kilius *et al.* 1984). In practice, most of our analyses for precious metals have been done at q = 5+ or 6+, well beyond the 3+ charge state where most, but perhaps not all (Anthony *et al.* 1991) potential molecular interferences disintegrate.

The first and simplest application of *molecular* secondary-ion analysis is the use of oxide or sulfide ions (*e.g.*, PdS^-) to achieve a higher yield than that of a recalcitrant monatomic ion. This was demonstrated by Teng *et al.* (1987), who used oxide negative ions in the measurement of Re and Os isotopes at the ppm level in meteorites.

The possibility that PGE occur in part within submicroscopic atomic-scale clusters in mafic magmas has been considered by Tredoux *et al.* (1991) and Barnes (1993). This implies that PGE distribution in magmas need not be entirely controlled by silicate and sulfide liquid immiscibility, and that PGE may occur in part, within both sulfide and silicate melts, as neutral metallic clusters of 100 atoms or less. This seems consistent with the common finding of metallic PGE-rich refractory phases as minute inclusions in early-crystallizing magmatic chromite. Early-forming PGM are commonly trapped within chromite (Talkington *et al.* 1984), and the host spinel may serve to buffer them from later postmagmatic alteration (Merkle 1992). In a lower-temperature hydrothermal environment, the work of Bakken *et al.* (1991) on gold ores from Nevada has demonstrated the presence of gold particles 20–200 Å across within arsenian pyrite. A possible index of the abundance of such clusters might be provided by an AMS survey of the ratios of atomic to molecular negative ions, *e.g.*, $Pd^-:Pd_2^-$.

The chemical elements show an orders-of-magnitude range in their propensity to form negative or positive, singly- or multiply-charged secondary ions. The variable formation of negative, monatomic secondary ions of the precious metals is reflected in the variation of detection levels achieved in routine analysis at IsoTrace (Table 1).

TABLE 1. ACCELERATOR MASS SPECTROMETRIC ANALYSIS OF GEOLOGICAL SAMPLES FOR PRECIOUS METALS

Element	*Isotope*	*3σ detection level (ppb element in 100 s)*	*Isotope relative abundance %*
Gold	^{197}Au	0.005	100
Platinum	^{196}Pt	0.10	25.3
Iridium	^{193}Ir	0.25	62.7
Osmium	^{188}Os	20	13.3
Silver	^{107}Ag	0.05	51.8
Palladium	^{106}Pd	4	27.3
Rhodium	^{103}Rh	0.50	100
Ruthenium	^{101}Ru	4	17.0

The '3σ detection levels' quoted in recent IsoTrace work are defined as that level of an element, referenced to a geostandard material prepared as a sulfide fire assay bead, which generates 3 counts in a given time, typically 100 s. In practice, the count times are varied according to need, and may thus be 10 s for gold or silver, 100 s for palladium and 250 s for osmium. Reference values are shown. Note that levels attained in a given 'run' depend on instrumental parameters, and especially the use of the 'quick-cool' to control the cesium primary beam-current. The elements are listed in the typical sequence of a 'run'.

CONCLUSIONS

The intrinsic specificity of AMS, engendered by its unique range of secondary ion formation, destruction, filtering and detection options, remains, to paraphrase Lovering (1973) on the wider context of SIMS, a formidable weapon for the geochemist. Natural laws dictate that the sensitivity of AMS cannot be obtained by any of the low-energy methods; recognition of this fact in the geochemical community should generate the support needed for its further development and availability to trace-element geochemists.

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