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Velocity-dependent isotope fractionation in secondary-ion emission

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The formation of secondary ions is subject to isotopic fractionation (differing ionization probabilities for two isotopes) that depends linearly on the inverse velocity of the ejected ions. Theoretically, such a correlation follows directly from an exponential dependence of the ionization probability P on v^{-1}, $P \propto \exp(-v_0/v)$. The parameter v_0, derived from the experiment, amounts to $\sim 2\times 10^6$ cm/sec for B, Si, and Ca ions.

The determination of isotope ratios was a very early and is still an important application of secondary-ion mass spectrometry (SIMS). With current instrumentation, isotope ratios can be measured to a precision of approximately one part per thousand (per mil) for many elements; this capability is widely used, for example, in isotope geology and cosmochemistry.[1,2] The accurate determination of isotopic abundances requires that the measurement itself does not introduce an uncontrolled bias, i.e., that the measured isotope abundances correspond to the actual ones in the sample. Unfortunately, this is not necessarily the case. Isotopic fractionation, the failure of measured isotope abundances to reproduce the actual abundances, accompanying sputtering, and secondary-ion formation has been well documented in several studies.[3-8] Surprisingly, despite the far-reaching importance of precise isotope determinations, few systematic investigations of the isotopic fractionation effects due to secondary-ion emission have been undertaken. Common to most previous studies of fractionation effects[4-8] is the finding that the isotopic fractionation depends in some way on the kinetic energy of the emitted secondary ions. Slodzian and co-workers[4,5] noted that the magnitude of isotopic fractionation exhibits a roughly inverse dependence on the secondary-ion energy and proposed a bond-breaking model to explain their observations. The interpretation of their data is, however, limited by the broad energy acceptance (20–60 eV) of their mass spectrometer.

With few exceptions, the probability P of an atom to be sputtered as an ion is found to increase with the magnitude of the secondary-ion emission velocity and an exponential dependence of P on v^{-1} is now favored on theoretical grounds:[9,10]

$$P \propto \exp(-v_0/v) \ , \tag{1}$$

where v_0 is a constant for a given sputtered ion-substrate system. (See, for example, Ref. 9 for a recent review of theories of secondary-ion formation.) Attempts to verify this relationship experimentally have produced ambiguous results. Yu[11] has reported results in agreement with Eq. (1), while other experiments[12] have suggested a power-law dependence on v.

Consider now two isotopes i and j of an element having masses M_i and M_j and assume $M_j > M_i$. Then the isotopic fractionation F_{ji} is the relative difference of the ionization probabilities of isotopes i and j, $F_{ji} \equiv (P_j - P_i)/P_i$ or, by using Eq. (1),

$$F_{ji} = \exp(-v_0/v_j)/\exp(-v_0/v_i) - 1 \ . \tag{2}$$

Replacing $v_j = v_i(M_i/M_j)^{1/2}$ and expanding Eq. (2) in a series of the exponential function yields

$$F_{ji} = 1 + \left[-\frac{v_0 M_0}{v_i} \right] + \cdots - 1 \ , \tag{3}$$

where $M_0 = (M_j/M_i)^{1/2} - 1$. Since M_0 is $\sim 10^{-2}$ and v_i is approximately equal to v_0 for the range of velocities investigated here (see below), second- and higher-order terms in Eq. (3) can be neglected and

$$F_{ji} \cong -\frac{v_0 M_0}{v_i} \ . \tag{4}$$

With the further approximation $M_0 \sim (M_j - M_i)/2M_i$, Eq. (4) is equivalent to the derivation of Δ_{ij} given by Slodzian and co-workers.[4,13] In what follows, we show that the measured isotopic fractionation F_{ji} for the elements B, Si, and Ca is linearly proportional to the inverse of the emission velocity v^{-1} and demonstrate that the experiments provide a precise determination of the parameter v_0 in Eqs. (1) and (4).

The experiments were carried out on the PANURGE ion microprobe (a modified Cameca IMS-3f) described in detail elsewhere.[14] Briefly, a 14.5-keV O^- primary beam of ~ 1 nA beam current was used for sputtering. Positive secondary ions emitted into a half-angle of $\leq 15°$ were collected and passed into the mass spectrometer. The instrument was operated at a mass resolving power $(M/\Delta M)$ ranging from 1200 (for B^+ isotopes) to 4500 (for Ca^+), sufficient to resolve all isobaric interferences, especially hydrides. Peak jumping between two or more isotopes was performed under automated field control. To permit precise measurements of ion velocities, the energy slit of the mass spectrometer was closed to transmit ions only within a ~ 2 eV window. The width of the energy window was calibrated using the known narrow energy spectra of molecular ions (e.g., Si_2O), while the zero of the energy scale was determined from the low-energy end point of the very steeply sloping energy spectra of all secondary ions. The estimated uncertainty in the energy calibration is ± 0.5 eV. The nonconducting samples showed slight charging and energy distributions were recorded before and after each set of isotope measurements at a given energy to control these effects; the shift of the energy spectrum due to charging was not more than 1 eV during a run. The kinetic energy (and therefore the velocity) of secondary ions was selected by offsetting the sample potential and keeping the other parameters of the instrument unchanged. Ion detection was by an electron multiplier; reported isotope ratios are corrected for dead-time counting losses.

Isotopic ratios for three elements were measured: $I(^{11}\mathrm{B}^+)/I(^{10}\mathrm{B}^+)$ from a tourmaline sample, $I(^{29}\mathrm{Si}^+)/I(^{28}\mathrm{Si}^+)$ from a P-doped silicon sample, and $I(^{44}\mathrm{Ca}^+)/I(^{40}\mathrm{Ca}^+)$ from a fluorite ($\mathrm{CaF_2}$) sample. The tourmaline and the fluorite sample were Au-coated (~200 Å) prior to analyses to minimize charge buildup during ion bombardment. Values of F_{ji} were derived from the measured secondary-ion intensity ratios (usually the mean of a set of 100 or more individual ratios) compared with the "true" abundance ratios of these isotopes in the sample. For B, this latter value ($[^{11}\mathrm{B}]/[^{10}\mathrm{B}]=4.0307$) was determined independently by thermal ionization mass spectrometry,[15] while for Si (Ref. 16) and Ca (Ref. 17) literature data were used, since these elements are known to exhibit only very small (a few per mil) abundance variations in terrestrial materials.[17] Note, however, that such deviations, if they were to occur, do not change the essential feature of the experiment, i.e., Eq. (4) will still be valid although v_0 would change slightly. All measurements were done under steady-state conditions, when the total flux of sputtered species (neutrals *and* ions) was identical to the bulk abundances.

Figures 1–3 depict the isotopic fractionation F_{ji} vs $1/v_i$ for B, Si, and Ca. In all cases, F_{ji} is plotted in per mil (i.e., measured values times 1000). For Ca, the data were normalized to one atomic mass unit (amu) to facilitate comparison. As in previous studies, a negative fractionation is found, i.e., a depletion of the *heavier* isotopes in the secondary-ion flux relative to the normal composition. This depletion increases with decreasing velocity of the ions. The errors given for F are $\pm 2\sigma_{\mathrm{mean}}$ of a set of 100 or more single ratios and range from 1–4 per mil. The errors for the velocity result from the uncertainties of the energy scale discussed above and its shift due to sample charging. In terms of energy, the uncertainty is in no case larger than ±1 eV. The straight lines are linear least-squares fits to the data. The correlation coefficients of these fits are 0.997, 0.998, and 0.995 for B, Si, and Ca, respectively. Clearly, the data are in excellent agreement with the linear relationship given in Eq. (4) and by inference can also be considered as a strong experimental support for the ex-

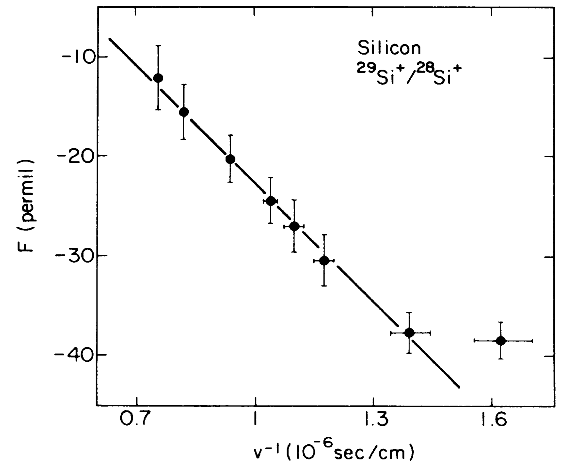

FIG. 2. Fractionation (in per mil) vs v_i^{-1} for Si^+ isotopes emitted from silicon.

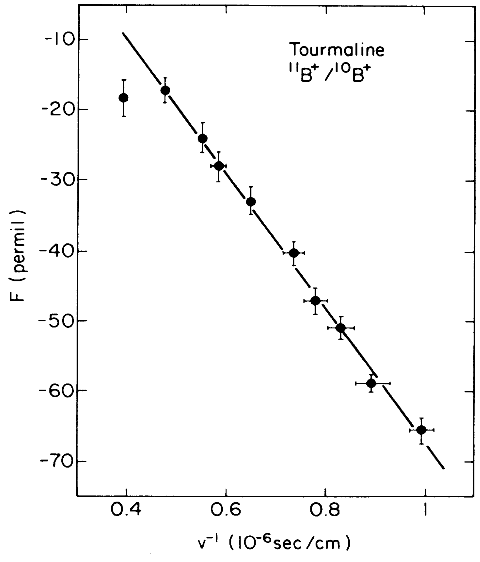

FIG. 1. Fractionation (in per mil) vs v_i^{-1} for B^+ isotopes sputtered from tourmaline with the chemical composition $\mathrm{Na(Li,Al)_3Al_6B_3Si_6O_{27}(OH,F)_4}$.

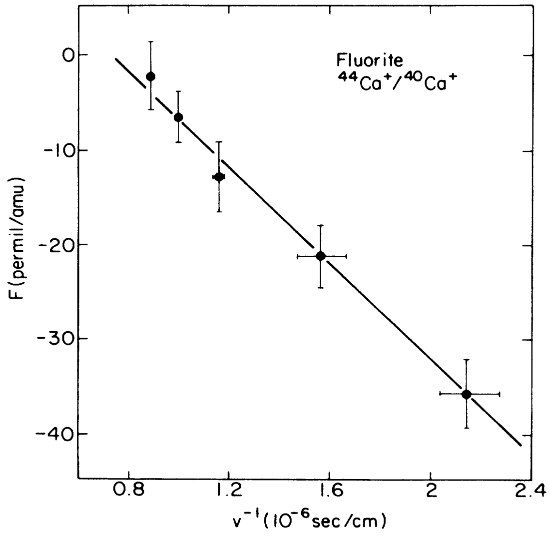

FIG. 3. Fractionation (in per mil/amu) vs v_i^{-1} for Ca^+ isotopes sputtered from fluorite ($\mathrm{CaF_2}$). Note the normalization of the measured F values to 1 amu.

ponential dependence of P on v given in Eq. (1). According to Eq. (4), the slope of the straight lines in Figs. 1-3 can be used to evaluate v_0. The respective values (in 10^6 cm/sec) are 2.0 for B , 2.3 for Si, and 2.1 for Ca.

Previous experiments[18] based on measured energy distributions of secondary ions and assumed spectra of neutral species according to the Thompson formula,[19] i.e., utilizing Eq. (1) directly, yielded similar values for v_0: $(2-3)\times10^6$ cm/sec for several transition metals.[18] This close agreement clearly supports our approach. Furthermore, since according to current theories[9,10] v_0 is related to the physical properties of the emitted ion and the substrate, some insight into these parameters might be expected from a precise evaluation of v_0 for a greater variety of elements.

It is worth noting that, according to theory, P is dependent on the velocity component *normal* to the surface.[9,10] Therefore, one might expect that any variation of this component by changing the accepted takeoff angle of secondary ions will have the same effects on F as variations via the emission energy. Unfortunately, our experimental setup is not well suited to check such dependence.

While the linear correlations between F and v^{-1} shown in Figs. 1-3 cover an energy range from $\sim$4-5 to 30 eV, it appears that at least for Si (cf. Fig. 2) deviations occur for lower energies . It must be noted that reliable measurements in this energy range (≤ 5 eV) are rather difficult because of the very steep slope (about a factor of 50 change in ion intensity per eV) of the energy spectra below the maximum. Furthermore, since F decreases rapidly at low energies, the finite resolution of the energy analyzer might induce a systematic error in this regime. Besides these potential instrumental problems, concern has been expressed[9,20] as to whether at low values the measured energy (velocity) is relevant at all. The velocity of charged particles leaving the surface might be expected to change due to the ion's exposure to attractive forces.[20] This effect will of course be most pronounced at low velocities and make the experimentally determined values differ from those relevant for the ionization process. In fact, deviation from Eq. (1) at low velocities have been observed in the experiment by Yu.[11] For ion emission from metals, simple image force corrections have been applied to the energy with some success.[18,21] We abstained from applying any corrections in view of the possible instrumental ambiguities mentioned above.

Preliminary measurements suggest that F levels off to a constant value at high velocities (cf. Fig. 1). Such a behavior also follows from Eq. (1) since P cannot exceed unity while the onset depends on the preexponential factor in (1). The constant value of F can be different from zero, because instrumental effects (e.g., mass discrimination in the electron multiplier) may also contribute to the measured F. Clearly, more precise experiments are needed to establish whether deviations from the linear correlation between F and v^{-1} at high energies are instrumentally induced or an intrinsic property of secondary-ion emission.

In summary, we have demonstrated that the process of secondary-ion formation induces a fractionation in the flux of emitted isotopes that is linearly dependent on the inverse velocity of the ions. This relation can be directly derived from current theories of secondary-ion emission. Extension of the present investigations to other elements and ion species (e.g., molecules) can be expected to improve further the understanding of secondary-ion formation.

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